VOL. XIV. [APRIL, 1892.] No. 4.

AMERICAN

CHEMICAL JOURNAL.

A REDETERMINATION OF THE ATOMIC WEIGHT OF CADMIUM.

BY H. N. MORSE AND H. C. JONES.

The fractional distillation of metals in a vacuum for the purpose of obtaining pure material for atomic weight determinations, which was first employed in this laboratory by Morse and Burton[1] in their work upon the atomic weight of zinc, was found to be as successful when applied to magnesium and cadmium as it had been with zinc. It was therefore decided to employ it in a redetermination of the atomic weights of those metals also. The work upon magnesium was undertaken by Burton and Vorce,[2] that upon cadmium by the authors of this paper.

At first we only intended to employ the very simple and direct method which had been used in the case of zinc and magnesium, *i. e.* the conversion of the metal into nitrate and then into oxide; but when our work was well advanced, there appeared a paper on the atomic weight of cadmium by Partridge,[3] who had also employed the distillation process for the purification of his metal. As there was some discrepancy between the results obtained by Partridge and by ourselves, we determined to extend the work so as to include one of the methods which had been used by him. Of the three methods used by Partridge, *i. e.* the conversion of the oxalate into oxide, the reduction of the sulphate to sulphide and the conversion of the oxalate into sulphide, the first was selected

[1] This Journal **10**, 311. [2] This Journal **12**, 219. [3] Am. J. Sci. **40**, 377.

as probably the best, because it is the simplest and because it gives somewhat more directly the relation of cadmium to oxygen. The uncertainties pertaining to the results obtained by all three of these methods, which are due to the fact that the question of the true atomic weights of carbon and sulphur is involved, have been discussed by Clarke.[1]

The material employed for the preparation of pure metal was obtained from Schuchardt. It was designated by him as "cadmium met. puriss. galv. reduc." This was placed in a combustion tube of glass and heated for a long time in a current of hydrogen, which had been purified by washing with both acid and alkaline solutions of potassium permanganate. In this way it was converted from the form of a powder into bars suitable for distillation in a vacuum. The subsequent treatment of the metal was the same as that employed for the purification of zinc.[2]

Partridge found his material pure after a second distillation, but we were much less fortunate. We could not satisfy ourselves that the metal was entirely free from arsenic until it had been five times redistilled.

It was then redistilled a sixth time. In each of the last two distillations the metal was kept for not less than twenty hours at a temperature just above the melting-point, with the expectation that if traces of arsenic were still present we should be able to find it in the thin incrustation which always collects upon the glass in the cooler end of the tube. In the last distillation nothing but cadmium was found in this incrustation. The sixth distillate, which was the material employed in this work, was examined spectroscopically by Professor Rowland and found to be free from all impurities which can be detected by that method.

The nitric acid used for dissolving the metal was purified as in the case of zinc,[3] by distilling the diluted acid from a flask against a large platinum dish and collecting it in a smaller one of the same metal. It gave no residue on evaporation.

The arrangement of the crucibles in which the metal was dissolved and finally weighed as oxide was similar to that employed in the determination of the atomic weight of zinc above referred to. It consisted of a small porcelain crucible, on the edge of which were placed short U-shaped platinum wires, to prevent the lid from

[1] This Journal **13**, 34.

[2] Loc. cit. We are much indebted to Dr. W. V. Metcalf, who prepared the pure metal.

[3] Loc. cit.

adhering to the crucible and to allow the vapors of oxides of nitrogen to escape, and a larger porcelain crucible in which the smaller one was placed. The glaze upon the outside of the larger crucible was removed by means of hydrofluoric acid, to prevent sticking when heated to a high temperature. These crucibles were weighed together and never separated during a determination. A second pair of crucibles of the same sizes and as nearly as possible of the same weights, but slightly lighter, was used as a tare. The crucibles which served as a tare were prepared in the same manner as the others. The glaze was removed from the outside of the larger one, while the inner one was furnished with platinum wires of the same weight as those of the first pair. The weight of the tare was made equal within less than a tenth of a milligram to that of the first pair, by adding to it small fragments of the same kind of porcelain. Both sets were treated as nearly as possible in the same manner. Whenever acid was added to one, an equal volume was placed in the other. They were likewise heated in every case to the same temperature and for the same length of time.

This method of weighing the containing vessels by means of properly prepared tares which are subjected to the same treatment throughout, was adopted because it rendered our weighings independent of the varying hygroscopic conditions of the air and made their reduction to the vacuum standard unnecessary. Another great advantage derived from this method of weighing by tares is the compensating of any errors due to impurities in the acid or resulting from the prolonged heating of the crucibles. The work at the balance was all done between one and five a. m., and all the precautions mentioned in the article on the atomic weight of zinc were observed. The methods of weighing by vibrations and upon both pans were employed throughout.

To prepare for a determination, the pair of crucibles and the tare were placed upon pieces of unglazed porcelain in larger crucibles of nickel, and heated for half an hour over the blast-lamp. The difference in weight was then ascertained, and the heating and weighing repeated. In every case the first difference found proved to be constant.

A piece of the metal weighing from two to three grams was cut from the bar with a polished and carefully cleaned cold-chisel. The portions which had come in contact with the chisel or with the air were removed with a specially hardened file, which had

also been cleaned with alcohol and ether. After weighing, the metal was placed in the inner crucible and treated with an excess of acid. A gentle heat was applied as long as any of the metal remained undissolved. The time required for this part of the operation was from twenty to forty hours. To remove the excess of nitric acid, the crucibles were placed in a porcelain cup which was surrounded by sand, and gently heated until the dried nitrate began to give off red vapors. They were then transferred to a similar bath containing iron filings instead of sand. Here they were heated by a single burner as long as any evidence of decomposition could be observed, and then by triple burners from six to eight hours. Finally, they were heated over the blast-lamp in a bath consisting of a nickel crucible, from two to three hours. To prevent contact between the outer porcelain crucible and the nickel, a piece of unglazed porcelain was placed in the bottom of the bath. To avoid any possible contact of the oxide with reducing gases from the flame, the nickel crucible was tightly forced into a hole cut in a board of asbestus. The heating over the blast was repeated until a constant weight was obtained. Usually three hours of blasting were sufficient, but in some cases four were necessary to bring the oxide to constant weight.

At the temperature of the muffle-furnace the oxide of cadmium attacks porcelain with great energy. For this reason we did not adopt the method employed by Morse and Burton for the final heating of the oxide of zinc. In every case, however, we assured ourselves of the completeness of the decomposition by testing the oxide with pure potassium iodide and hydrochloric acid for the presence of the oxides of nitrogen.

We give below the results of ten successive determinations:

	Cadmium.	Cadmium Oxide.	O = 16. At. Wt. Cd.	O = 15.96. At. Wt. Cd.
I	1.77891	2.03288	112.070	111.790
II	1.82492	2.08544	112.078	111.798
III	1.74688	1.99626	112.078	111.798
IV	1.57000	1.79418	112.053	111.773
V	1.98481	2.26820	112.061	111.781
VI	2.27297	2.59751	112.059	111.779
VII	1.75695	2.00775	112.086	111.806
VIII	1.70028	1.94305	112.059	111.779
IX	1.92237	2.19679	112.083	111.803
X	1.92081	2.19502	112.078	111.798
	18.47890	21.11708	112.0705	111.7905

Maximum, 112.086
Minimum, 112.053
Mean, 112.0705
Difference, .033

The relation established between the total cadmium used and the total oxide found was:

Cd : CdO = 18.47890 grams : 21.11708 grams ;
or Cd : O = 18.47890 grams : 2.63818 grams ;
from which if O = 16, at. wt. Cd = 112.0706,
if O = 15.96, " " " = 111.7904.

The result obtained agrees more closely with those of von Hauer and Lenssen than with those of any other experimenter.

	Von Hauer. Nine Determinations.	Lenssen. Three Determinations.	Our Work. Ten Determinations.
Max.	112.121	112.304	112.086
Min.	111.796	111.911	112.053
Mean,	111.940	112.067	112.0705
Diff.	.325	.393	.033

Oxalate Method.

Great care was taken to prepare a specimen of oxalic acid which should give no residue on ignition. A large quantity of the acid was agitated with cold water to saturation. The solution thus obtained was evaporated to crystallisation. The product was twice recrystallised in the same manner. It was then heated for two days with a fifteen per cent. solution of hydrochloric acid. The crystals which separated from the acid on cooling were afterwards recrystallised, twice from ninety-five per cent. alcohol and twice from pure ether. The material was then dissolved in pure water and the solution boiled until all odor of ethyl oxalate had disappeared. The crystals which separated from this solution were again crystallised from pure water. The acid thus purified gave no residue after ignition.

All the water used in connection with the oxalate method was purified in the manner previously described for the preparation of pure nitric acid, *i. e.* by condensing its vapor upon cold platinum.

The metallic cadmium was dissolved in pure nitric acid and the excess of acid evaporated off. The nitrate was dissolved in water and treated with a little less than an equivalent amount of oxalic

acid in solution. The oxalate which separated after a few moments was collected on a porcelain filter, washed free from nitric acid and dried in an air-bath at 150° C. for twenty hours. In consequence of the hygroscopic nature of the dried oxalate it was necessary to make all weighings in closed vessels. Portions of the salt sufficient for single determinations were placed in glass-stoppered weighing tubes, which had been tared against other similar glasses and dried at 150° C. to constant weight. This last stage of the drying process usually required about fifteen hours. The crucibles used in converting the oxalate into oxide were the same as those previously described. After pouring the oxalate from the tube into the weighed crucibles, the tube and tare were again dried to constant weight at 150° C. This was done to avoid any error resulting from the absorption of water during exposure to the air by the small quantity of oxalate adhering to the inside of the weighing glass. The pair of crucibles containing the weighed oxalate was placed in a larger crucible and heated in an asbestus-covered air-bath. The temperature was increased very slowly until the material began to turn to a brown color on the outer edge. From this point the temperature was kept as nearly constant as possible until the whole mass had become uniformly brown in color. After cooling, the material was completely dissolved in nitric acid and then evaporated to dryness and converted into oxide exactly as in the preceding method.

The table given below contains the results of five successive determinations. The weights of the oxalate given are corrected for the difference in specific gravity between the salt and weights, on the basis of sp. gr. 8.4 for brass and 21 for platinum weights, and sp. gr. 3.31 for oxalate.

	CdC_2O_4.	CdO.	O = 16. C = 12.001. At. Wt. Cd.	O = 16. C = 12.003. At. Wt. Cd.	O = 15.96. C = 11.971. At. Wt. Cd.	O = 15.96. C = 11.973. At. Wt. Cd.
I	1.53937	.98526	112.026	112.033	111.746	111.753
II	1.77483	1.13582	111.981	111.988	111.701	111.708
III	1.70211	1.08949	112.049	112.056	111.769	111.776
IV	1.70238	1.08967	112.051	112.058	111.771	111.778
V	1.74447	1.11651	112.019	112.026	111.739	111.746
	8.46316	5.41675	112.025	112.032	111.745	111.752
	Maximum,		112.051		112.058	
	Minimum,		111.981		111.988	
	Mean,		112.025		112.032	
	Difference,		.070		.070	

The values assigned to carbon in the last two columns were obtained thus: if when O = 16 C = 12.001, when O = 15.96 C = 11.971; if when O = 16 C = 12.003, when O = 15.96 C = 11.973.

The ratio established between the oxalate and oxide is:

$$CdC_2O_4 : CdO = 8.46316 \text{ grams} : 5.41675 \text{ grams},$$

whence, if	O = 16	O = 16	O = 15.96	O = 15.96
and	C = 12.001	C = 12.003	C = 11.971	C = 11.973
the	at. wt. Cd is	at. wt. Cd.	at. wt. Cd.	at. wt. Cd.
	112.025	112.032	111.745	111.752

Our results agree much more closely with Lenssen's than with Partridge's, as will be seen from the following statements based on the atomic weights of 16 for oxygen and 12.003 for carbon:

Lenssen.	Partridge.	Our Work.
112.043	111.816	112.032

or, on atomic weights of 16 for oxygen and 12.001 for carbon:

Lenssen.	Partridge.	Our Work.
112.036	111.809	112.025

We regard the number 112 0706, which was obtained by converting weighed portions of metal into oxide, as more reliable than the numbers 112.025 or 112.032, obtained by the conversion of weighed quantities of oxalate into oxide.

The first method is exceedingly simple and gives directly the relation of cadmium to oxygen. The substances weighed are not hygroscopic.

The second method is more complicated and involves the question of the true atomic weight of carbon. The oxalate is strongly hygroscopic. Moreover, when it is reduced to oxide by heat there is great danger of loss from reduction to and volatilisation of metal.

Historical.

We append a brief, chronologically arranged account of the determinations of the atomic weight of cadmium which have been made up to the present time. The methods which have been employed are:

1. Conversion of the metal into oxide (Stromeyer).
2. Reduction of the sulphate to sulphide (von Hauer and Partridge).
3. Determination of the chlorine in the chloride (Dumas).

4. Conversion of the oxalate into oxide (Lenssen and Partridge).
5. Determination of bromine in the bromide (Huntington).
6. Conversion of the oxalate into sulphide (Partridge).

1818. Stromeyer: Schweigger's Journ. **22**, 366.

Method: conversion of the metal into the oxide.

100 parts of metal combine with 14.352 parts of oxygen;

or Cd: CdO = 6.9677 : 7.9677. O : Cd = 16 : 111.483.

Stromeyer gives no description of his methods; it is therefore impossible to estimate the value of his work.

1857. Von Hauer[1]: Journ. f. prakt. Chem. **72**, 338.

Method: reduction of sulphate to sulphide. Number of determinations, nine.

A total of 64.2051 grams of sulphate gave 44.4491 grams of sulphide.

Whence, if oxygen = 16 and sulphur = 32.059, cadmium = 111.935.

Highest individual result,	112.121
Lowest " "	111.796
Mean of all results,	111.940
Difference between highest and lowest result,	0.325

The sulphate obtained by repeated crystallisations was acidified and treated with hydrogen sulphide. The thoroughly washed sulphide was dissolved in hydrochloric acid, and the cadmium precipitated by ammonium carbonate. The carbonate was carefully washed and converted by heat into oxide. To remove any traces of chloride, the oxide was washed for a long time with boiling water and again ignited. It was then dissolved in dilute sulphuric acid and several times recrystallised. Before each recrystallisation, the sulphate was gently ignited in order to remove any excess of sulphuric acid. The sulphate was finely powdered, dried at about 200° C. and heated, gently at first, but afterwards to redness in a porcelain boat, in an atmosphere of hydrogen sulphide. The sulphide of cadmium was tested in every case for unreduced sulphate.

Von Hauer appears to have taken great care in the purification of his sulphate, and the largeness of the quantities employed in the individual determinations (from six to eight grams) tended to diminish the effect of experimental errors.

[1] In the eighth determination of von Hauer, the amount of cadmium sulphate used must have been 5.8245 grams, and not 7.8245 grams as given.

The weighing of the anhydrous sulphate and the sulphide in open vessels must have introduced some error. But the most serious source of error, as it appears to us, is the heating of the sulphate in porcelain, to redness, while undergoing reduction. It seems probable that some of the sulphate was decomposed to oxide, which, according to our experience, attacks porcelain with considerable energy at that temperature. The effect of such action would be to lower the atomic weight found.

1859. Dumas: Ann. Chim. Phys. (3), **55**, 158.

Method: determination of chlorine in the chloride; number of determinations, six.

A total of 23.0645 grams of cadmium chloride was equivalent to 27.173 grams of metallic silver.

Whence, if chlorine = 35.45 and silver = 107.93. cadmium = 112.322.

Highest individual result,	112.759
Lowest " "	111.756
Mean of all results,	112.241
Difference between highest and lowest result,	1.003

Metallic cadmium was dissolved in boiling hydrochloric acid. The solution was evaporated to dryness and the residue kept in the molten condition in an atmosphere of hydrochloric acid gas for five or six hours. Dumas gives no further particulars as to his procedure. He states, however, that the chloride employed in the first three determinations was of a brown color in places, while that used in the last three was white throughout and perfectly soluble in water, having been prepared from metal supposed to be pure. The results of the first set were: 112.322, 112.347, 112.759; average, 112.476.

The results of the second were: 111.756, 112.135, 112.130; average, 112.007.

It is clear that the first three determinations have little value, while Dumas himself calls attention to a possible source of error pertaining to all of his results. He states that during the heating of the chloride in gaseous hydrochloric acid, a third, a half, or two-thirds of the salt were lost by volatilisation, thus concentrating any less volatile impurities in the residue, which was the material employed in his work.

1860. Lenssen: Jour. f. prakt. Chem. **79**, 281.

Method: conversion of the oxalate into oxide. Number of determinations, three.

A total of 1.5697 grams of oxalate gave 1.0047 grams of oxide. Whence, if oxygen = 16 and carbon = 12.003, cadmium = 112.043.

Highest individual result,	112.304
Lowest individual result,	111.911
Mean of all results,	112.067
Difference between highest and lowest result,	0.393

A solution of repeatedly recrystallised cadmium chloride was treated with an excess of pure oxalic acid. The precipitate was filtered off, very carefully washed, and dried for a long time at 150° C. The weighed salt was decomposed at as low a temperature as possible, in a porcelain crucible. The residue was moistened with pure nitric acid, dried at a gentle heat, and finally strongly ignited.

Lenssen does not state how his nitric and oxalic acids were prepared in the pure condition, neither does he describe any precautions taken to avoid errors resulting from the strongly hygroscopic nature of the dried oxalate. The large differences between the highest and lowest results (nearly .4 of a unit) may have been due to the absorption of water by the oxalate and to the small quantity of material used.

1882. Huntington and Cooke: Proceedings Amer. Acad. **17**, 28.

Methods: (1) determination of bromine in the bromide; (2) determination of the amount of silver required to precipitate the bromine in the bromide.

Number of determinations by each method, eight.

In the first series, a total of 23.3275 grams of cadmium bromide gave 32.2098 grams of silver bromide. Whence, if silver = 107.93 and bromine = 79.95, cadmium = 112.239.

Highest result,	112.290
Lowest result,	112.169
Difference between highest and lowest results,	0.121

In the second series a total of 28.6668 grams of cadmium bromide were equivalent to 22.7379 grams of silver. Whence, if silver = 107.93 and bromine = 79.95, cadmium = 112.245.

Highest result,	112.32
Lowest result,	112.18
Difference between highest and lowest results,	0.14

The commercial metal was dissolved in pure hydrochloric acid, precipitated by hydrogen sulphide, and the sulphide thoroughly washed with hot water. The sulphide was then dissolved in hydrochloric acid, the cadmium precipitated by ammonium carbonate, and the precipitate digested with a large excess of the reagent. The above processes were repeated. Lastly, to remove any traces of chloride, the carbonate was dissolved in pure hydrobromic acid and again precipitated as carbonate. The bromide was prepared by dissolving this carbonate in pure hydrobromic acid and subliming the dried product in a current of pure carbon dioxide.

The experimental part of this work appears to have been carefully done, but the result is strikingly higher than that obtained by any other experimenter, if we exclude the result of Dumas' first series, which, as we have already pointed out, is of but little value.

1890. Partridge:[1] Amer. Jour. Sci. (3), **40**, 377.

Methods: (1) conversion of the oxalate into oxide; (2) reduction of sulphate to sulphide; (3) conversion of the oxalate into sulphide. Number of determinations by each method, ten.

The results of the three series, based on total quantities of materials used and obtained, employing whole numbers for the atomic weights of carbon and sulphur, as was done by Partridge, are given below:

1st series, 12.66368 grams CdC_2O_4 gave 8.10031 grams CdO, at. wt. Cd 111.805.

2d series, 15.93505 grams $CdSO_4$ gave 11.02691 grams CdS, at. wt. Cd 111.786.

3d series, 16.85228 grams CdC_2O_4 gave 12.12906 grams CdS, at. wt. Cd 111.806.

Difference, .02.

But as Clarke[2] has pointed out, if the more probable values for carbon and sulphur are employed in the calculation of the results, the remarkable agreement between the different series disappears. If we employ the numbers 12.001 for carbon and 32.058 for sulphur (Clarke), the results are, for

[1] The following corrections are to be made in the results as published:
(1) Series: Total cadmium oxide found was 8.10031 grams, and not 8.10027 grams.
(2) Series: Total sulphide found was 11.02691 grams, and not 11.69717 grams.
(3) Series: Sulphide found in eighth experiment, 1.46517 grams, and not 1.45617 grams.

[2] This Journal **13**, 34.

1st series,	111.8036
2d "	111.7271
3d "	111.6054
Difference,	.1982

If we employ the numbers 12.003 for carbon and 32.059 for sulphur (Meyer and Seubert), the results are for,

1st series,	111.816
2d "	111.727
3d "	111.610
Difference,	.206

Of the three methods employed by Partridge, we are prepared at present to speak only of the first. As we have already stated, there are certain unavoidable objections to the method, *i. e.* the hygroscopic nature of the oxalate, the danger of loss of metal during the conversion of the salt into oxide, and the necessity of introducing the atomic weight of another element than oxygen into the calculation. This last objection applies to the second method also, and with double force to the third.

In general we should say that, according to our experience, two rapid distillations, such as are described by Partridge, do not suffice for the purification of the metal.

The following table contains a summary of the results obtained to date. When two values are given for any series of determinations, the first is calculated from the total material used and the total product found; the second is an average of the results of the separate determinations. All the results are calculated on the basis of oxygen = 16, unless otherwise stated:

	Atomic Weight of Cadmium.
1818, Stromeyer,	111.483
1857, von Hauer (S=32.059),	111.935 }
" "	111.940 }
1859, Dumas, 1st series (Ag=107.93, Cl=35.45),	112.476
2d " " " " "	112.007
1860, Lenssen (C=12.003),	112.043 }
" "	112.067 }
1882, Huntington and Cooke, 1st series (Ag=107.93, Br=79.95)	112.239
2d series, (Ag=107.93, Br=79.95),	112.245

1890, Partridge,	1st series (C=12, S=32), .	111.805
	2d " " " " " . .	111.786
	3d " " " " " .	111.806
Partridge,	1st series (C=12.001, S=32.058),	111.8036
	2d " " " " "	111.7271
	3d " " " " "	111.6054
Partridge,	1st series (C=12.003, S=32.059),	111.816
	2d " " " " "	111.727
	3d " " " " "	111.610
1892, Morse and Jones,	1st method, . . .	112.0706
	1st " (O=15.96)	111.7904
	2d " (C=12.001)	112.025
	2d " (C=12.003)	112.032
	2d " (O=15.96, C=11.971), .	111.745
	2d " (O=15.96, C=11.973), .	111.752

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

NOTE ON CRYSTALS OF METALLIC CADMIUM.

By George H. Williams.

No reliable crystallographic description of the element cadmium seems thus far to have appeared—a fact due to the difficulty in obtaining suitable material. The crystals submitted to me by Prof. Morse for examination, although not capable of yielding entirely satisfactory results, are nevertheless of much interest.

In 1852 G. Rose noted the fact that distilled cadmium collected at the neck of the retort in drops which solidified as complex polyhedral aggregates,[1] similar to those formed by zinc.[2] In 1874 Kammerer encountered the same aggregates, which he explained as complicated isometric combinations.[3] This opinion was cited in 1881 by Rammelsberg.[4] In 1884 Brögger and Flinck stated that, in their opinion, zinc, magnesium and probably cadmium were, from analogy with beryllium which they had studied, hexagonal and holohedral.[5] This supposition has already been

[1] Pogg. Ann. **85**, 293 (1852).
[2] Ib. Cf. This Journal **11**, 219 (1889).
[3] Ber. d. chem. Ges. **7**, 1724 (1874).
[4] Handb. d. krystallographisch-physikalischen Chemie **1**, 184.
[5] Brögger und Flinck: Zeitschr. f. Kryst. **9**, 236 (1884).

substantiated in the case of the two former elements,[1] while the present material leads to the same result for the last named.

The cadmium crystals were produced, as described in the paper by Prof. Morse and Mr. Jones, in the same manner as were those of zinc and magnesium measured before, viz. by distillation in a vacuum. The appearance of the tubes thus obtained was closely like that in the other cases. The polyhedral aggregates were abundant and reached considerable dimensions. The crystallising force of the cadmium, however, seems to be less, so that the only crystals suitable for measurement were extremely minute. The largest individuals were barrel-shaped, like those of zinc, and resemble little piles of basal plates. Their side planes are not infrequently uneven and bent, probably as the result of the softness and great ductility of the metal.

The most minute crystals alone show pyramidal planes of comparative perfection. These are well suited for a microscopic examination, but their small size renders their measurement on a reflecting goniometer a matter of difficulty. After a careful search two crystals were secured, which, although they had a diameter of only one-third of a millimeter, from their microscopic appearance promised good results. Their planes, however, were found to give compound reflections and a somewhat disappointing variation in corresponding angles.

On the best crystal three zones were measured as follows (normal angles):

Zone I.	Zone II.	Zone III
$0001 : 01\bar{1}1 = 62° 35'$	$0001 : 10\bar{1}1 = 62° 4'$	$0001 : 1\bar{1}01 = 62° 29'$
$0001 : 01\bar{1}0 = 89° 50\frac{1}{2}'$,		
$0001 : 01\bar{1}\bar{1} = 118° 57'$	$0001 : 10\bar{1}\bar{1} = 118° 28'$	

The second crystal was much less satisfactory, since values for the angle between the base and pyramid, $(0001) : (01\bar{1}1)$, were obtained which varied all the way from 61° 2′ to 63° 43′. These measurements must therefore be regarded as of little or no value. If we average the readings for this angle on the first crystal we obtain 62° 23′, corresponding to the axial ratio $a : c :: 1 : 1.6554$.

A comparison between the axial ratios of the four rhombohedral and four holohedral hexagonal elements gives the following :

[1] Williams and Burton: This Journal **11**, 225 (1889). Ib. **12**, 225 (1890).

Rhombohedral:

Bismuth, $a : c = 1 : 1.3035$ (G. Rose, 1849).
Antimony, $a : c = 1 : 1.3235$ (Laspeyres, 1875).
Tellurium, $a : c = 1 : 1.3298$ (G. Rose, 1849).
Arsenic, $a : c = 1 : 1.4025$ (Zepharovich, 1875).

Holohedral:

Zinc, $a : c = 1 : 1.356425$ (Williams and Burton, 1889).
Beryllium, $a : c = 1 : 1.5802$ (Brögger, 1884).
Magnesium, $a : c = 1 : 1.6202$ (Williams, 1890).
Cadmium, $a : c = 1 : 1.6554$ (Williams, 1891).

Zinc appears from its axial ratio to belong rather to the rhombohedral group, and this is the only one of the last four elements upon which the faintest indication of any divergence from a holohedral development of all of its forms has been observed. On crystals of this substance there is an occasional rhombohedral alternation of the faces of certain of the pyramids, although the crystals otherwise appear to be holohedral.[1]

The crystals of cadmium, like those of magnesium, show only the three forms oP (0001), P ($10\bar{1}1$), and ∞P ($10\bar{1}0$). Brögger and Flinck observed on beryllium the additional forms $\infty P2$ ($2\bar{1}\bar{1}0$) and $\frac{1}{2}P$ ($20\bar{2}1$); while upon zinc a large number of forms in the zone of the unit pyramid occur. Not infrequently the cadmium crystals show a tendency toward a hemimorphic development. This is plainly seen when a large number of them are examined together under the microscope. The little barrel-shaped crystals are mostly attached by their sides, and yet one of their ends is often broader than the other. Sometimes they taper nearly to a point, quite like greenockite crystals.

The cohesion phenomena of cadmium are similar to those of zinc, but are still more striking. When a crystal is sharply focused under the microscope and then gently pressed on the side with the point of a needle, an unbroken pyramidal face is seen to suddenly become striated parallel to the basal plane, as though a gliding in the basal section took place. Some of these crystals were kindly examined by Prof. Otto Mügge of Münster, Germany, who has added so much to our knowledge of the cohesion phenomena in crystals. He has written me in regard to his observations as follows: "The cadmium crystals, as far as their gliding phenomena are concerned, behave quite like zinc. If a crystal is

[1] This Journal **11**, 224 (1889). Pl. 2, Fig. 8.

carefully loosened and then squeezed with a pair of pincers, it is easy to see that the smooth surface where it was attached to the glass becomes striated parallel to oP (0001), and that at the same time two other sets of striations are produced which meet at an angle of about 85° and intersect the trace of the basal plane at about 47½°. The plane of attachment was selected for observation because it was smoother than the pyramidal faces. In the above case this plane has the position of a steep pyramid, inclined to the base at an angle of about 100°. The oblique sets of striations appear to represent gliding planes parallel to the unit pyramid faces (2P, $(10\bar{1}2)$ of Rose), as is the case with zinc. Whether the horizontal striations were due to gliding parallel to the base I could not certainly decide. Many of the crystals appear, when pinched, to be completely overturned, in which cases ordinary bending accompanies gliding, as in the case of gold, etc. This is shown by the fact that both faces and striations become rounded."

PETROGRAPHICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

Contribution from the Chemical Laboratory of Clark University, Worcester, Mass.

ON THE ETHERS OF QUINONE-OXIME (NITROSOPHENOL).

FIRST PAPER.

BY J. L. BRIDGE.

Some time ago H. Goldschmidt[1] proved that α-nitroso-β-naphthol and β-nitroso-α-naphthol were both oximes of β-naphthoquinone, $C_6H_4\begin{<}\begin{matrix}CO\\CH=CH\end{matrix}\begin{>}CO$, as follows:

1. Both these substances give on treatment with hydroxylamine the same dioxime-anhydride, $C_6H_4\begin{<}\begin{matrix}C=N\\CH=CH\end{matrix}\begin{>}\begin{matrix}C=N\\O\end{matrix}$.

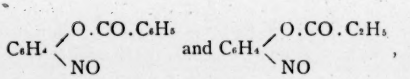
[1] Ber. d. chem. Ges. **17**, 801; **18**, 571 and 2224.

2. The ethers, obtained by treating the silver salts of these two substances with alkyl iodides, give on reduction amido-naphthols, hence the alkoxy groups cannot be present in the form of phenol ethers.

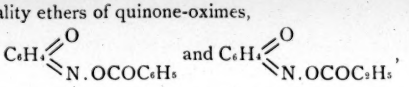
3. β-Naphthoquinone gives with α-methyl-hydroxylamine, $CH_3O.NH_2$, a substance, $C_6H_4\begin{<}{CO}{CH=CH}\diagup C=NO.CH_3$, which is identical with the methyl ether obtained by treating silver β-nitroso-α-naphthol with the methyl iodide.

That para-nitroso-α-naphthol is an oxime of α-naphthoquinone, $C_6H_4\begin{<}{CO}{CO}\diagup\diagdown{CH}{CH}$, is rendered probable by the fact that it is obtained from this quinone by means of hydroxylamine[1] (one molecule); in this case, however, further proofs are wanting. The same is true of ordinary para-nitroso-phenol. The latter substance is at the present time still regarded as a tautomeric compound, *i. e.* it seems to show a twofold chemical behavior, at times reacting as a nitroso-phenol, $C_6H_4\begin{<}{NO\ (1)}{OH\ (4)}$, and at other times like a quinone-oxime, $C_6H_4\begin{<}{N.OH\ (1)}{O\ \ (4)}$. For this there is, however, no positive evidence, and indeed nitroso-phenol, owing to its instability, has as yet been very little studied. I have therefore undertaken a study of this substance under the direction of Dr. Nef, with the object of obtaining ethers of it; and although both Ter Meer[2] and H. Goldschmidt[3] have stated that they obtained negative results in this direction, it was found that both silver- and sodium-nitroso-phenol react with alkyl iodides and acid chlorides, giving ethers of nitroso-phenol whose constitution was definitely proved to be as follows: $C_6H_4\begin{<}{O}{N.OR}$, *i. e.* the ethers are quinone oxime-ethers. It was also found that the benzoyl- and ethyl-carbonic ethers which Walker[4] obtained in 1884 and describes as phenol-ethers,

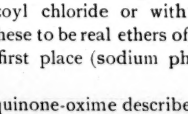
[1] Ber. d. chem. Ges. **17**, 2064. [2] Ibid. **8**, 625. [3] Ibid. **18**, 2226. [4] Ibid. **17**, 400.

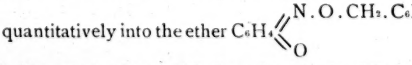


are in reality ethers of quinone-oximes,



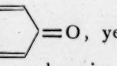
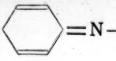
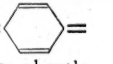
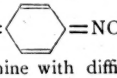
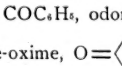
so that at present not a single reaction shown by nitroso-phenol can be construed as tending to show that this substance is a tautomeric compound. The ethers obtained by Walker were made by treating sodic phenolate with amyl nitrite and heating the resulting sodic nitroso-phenolate with benzoyl chloride or with chlorocarbonic ether. Walker supposed these to be real ethers of nitroso-phenol, because the sodium in the first place (sodium phenolate) was bound to the phenol group.

The ethyl and methyl ethers of quinone-oxime described in this paper are very remarkable substances; they no longer resemble nitroso-phenol in the least, but are yellow, strong-smelling substances, very volatile with steam, and show a very close resemblance in every particular to benzoquinone. Like it they form addition-products with the halogens;[1] the methyl ether, for instance, gives a colorless dibromide,  , which is not affected by fuming nitric acid.

The conclusive proof that the ethers obtained are not ethers of nitroso-phenol but of quinone-oxime is as follows: α-benzyl-hydroxylamine, $C_6H_5.CH_2-O-NH_2$, (one molecule) converts quinone quantitatively into the ether  , which is identical in every respect with the ether obtained from sodic or silver nitroso-phenol and benzyl chloride.

The results obtained also show that the properties and stability of quinone and its derivatives depend entirely on the negative or positive condition of the molecule,[2] and this explains the entirely different properties of the following substances which are all analogously constituted:

[1] This Journal **12**, 483. Ibid. **13**, 424. [2] Cf. Nef: Ann. Chem. (Liebig) **266**, 52.

Quinone, O=  =O, yellow, volatile, pungent odor, adds 4 atoms chlorine or bromine; quinone-oxime methyl ether, O=  =N—OCH_3, yellow, volatile, strong odor, adds 2 atoms bromine; quinone-oxime benzoyl ether, O=  = N—O.COC_6H_5, odorless, almost colorless, like nitroso-phenol; quinone-oxime, O=  =NOH, colorless, solutions green, adds 2 atoms bromine with difficulty; quinone-dichlor-diimid, Cl.N=  =NCl, colorless, odorless, very stable, does not add bromine.

Quinone-oxime methyl ether, $C_6H_4{=}{}^{O\ (1)}_{NOCH_3\ (4)}$.—The nitroso-phenol used in the following experiments was obtained as follows: 50 grams phenol, 25 grams sodium hydroxide, 45 grams sodic nitrite were dissolved in 1200 cc. of water and the solution cooled to 7°–8°. Thereupon 700 cc. dilute sulphuric acid (1 : 5) were added gradually, the vessel being cooled and shaken thoroughly during this operation. After two hours the nitroso-phenol which had separated out was filtered off and washed with ice-water, and then purified by dissolving in ether and treating in the cold with animal charcoal. On concentrating the etherial solution nitroso-phenol crystallises out in pale yellow needles which, if dried quickly, can be kept without change.

Silver nitroso-phenol was made by dissolving 1 gram of nitroso-phenol in sodic hydroxide (from 0.16 gram sodium) and pouring into a solution of silver nitrate (1.6 grams) in 300 cc. of water. The gelatinous dark-brown salt, which has been analysed by Ter Meer,[1] was filtered off, well washed, dried on clay plates and then at 75°.

The silver salt thus obtained was suspended in a small amount of absolute ether, and 1½ times the calculated amount of methyl iodide added, the solution being cooled if necessary. The mixture must not be warmed, and after standing for an hour or longer is

[1] Ber. d. chem. Ges. **8**, 624.

filtered and the etherial filtrate allowed to evaporate spontaneously. There is left a dark-brown, tarry mass which is digested with hot ligroin (boiling point 70°–80°), which extracts the methyl ether but leaves the tar behind. The ligroin solution is treated with animal charcoal until it becomes bright yellow in color, and on concentration a substance separates out in flat yellow needles which, recrystallised again, is pure and melts sharply at 83°.

0.1362 gram substance,[1] dried over sulphuric acid in a vacuum, gave 0.3070 gram CO_2 and 0.0664 gram H_2O.

0.1560 gram substance gave 14.3 cc. moist nitrogen at 22° and 748.2 mm.

	Theory for $C_7H_7NO_2$.	Found.
C	61.35	61.46
H	5.11	5.42
N	10.21	10.24

The methyl ether has a strong and pleasant etherial odor, is readily volatile with steam: if not quite pure it, like quinone, decomposes quickly, turning first green and then dark-brown. The substance is very readily soluble in organic solvents and hot water; it dissolves in considerable amount in cold water and ligroin.

This same substance is formed by warming gently a solution of sodic nitroso-phenol (made from nitroso-phenol and sodium ethylate) in methyl alcoholic solution with methyl iodide. The color of the solution changes from brown to dark-red, and a dark-red substance separates out in needles[2] (yield always about 0.2 gram from 1 gram nitroso-phenol taken) which is probably a polymeric nitroso-phenol. It is insoluble in organic solvents, but dissolves in caustic alkalies and ammonia with deep-red coloration, and is precipitated unchanged therefrom by means of acids or carbon dioxide. It does not melt but begins to decompose at about 250°. Repeated analyses were made, but no constant figures were obtained, as the substance seems to burn with enormous difficulty. The following reactions shown by the substance make it probable, however, that it is a polymeric nitroso-phenol: nitric acid (sp. gr. 1.4) converts it quantitatively into 1.2.4.-dinitrophenol[3] (m. p. 114°). Tin and hydrochloric acid reduce it to para-

[1] All the analyses in this paper were carried out by mixing the substance with the copper oxide.

[2] Cf. Ter Meer: Ber. d. chem. Ges. **8**, 625.

[3] Laurent: Ann. Chem. (Liebig) **43**, 213; Körner: Ztschr. Chem. 1868, 322.

amido-phenol (m. p. 180°), which was further proved by the conversion of this substance into quinone and quinone chlor-imid (m. p. 84.5°).

The above alcoholic filtrate contains, besides much tarry matter, quinone-oxime methyl ether, which was obtained by allowing the solution to evaporate spontaneously and extracting the residue with ligroin.

Quinone-oxime methyl ether dibromide, $C_6H_4\begin{matrix}=N.OCH_3\\=O\end{matrix}$, Br_2.—The methyl ether just described, when treated in chloroform solution with bromine (one molecule), is quantitatively converted into a dibromide. The absorption of the bromine is complete in half an hour and no hydrobromic acid is noticed. The solution is then allowed to evaporate spontaneously, and the residue, which is slightly colored, purified by dissolving twice in fuming nitric acid and pouring this solution into ice-water. The substance thus treated is colorless, and crystallises from chloroform in four-sided plates, which when heated begin to soften at 113° and melt completely at 118° without decomposition.

0.2820 gram substance, dried over sulphuric acid in a vacuum, gave 0.2962 gram CO_2 and 0.0676 gram H_2O.

0.1548 gram substance gave 0.1976 gram AgBr (Carius).

	Theory for $C_7H_7NO_2Br_2$.	Found.
C	28.57	28.64
H	2.36	2.66
Br	53.88	54.26

Quinone-oxime ethyl ether, $C_6H_4\begin{matrix}=N.OC_2H_5\\=O\end{matrix}$.—This ether is obtained like the methyl ether by treating the silver salt of nitroso-phenol with ethyl iodide. Crystallised from ligroin it is obtained in yellow rhombic or in hexagonal plates, melting at 30° and having a strong etherial odor.

0.1058 gram substance, dried over sulphuric acid in a vacuum, gave 0.2472 gram CO_2 and 0.0608 gram H_2O.

	Theory for $C_8H_9NO_2$.	Found.
C	63.58	63.71
H	5.96	6.38
N	9.27	9.31

The ethyl ether is easily volatile with steam; it dissolves readily in all solvents, but is least soluble in cold water and ligroin, and owing to its low melting-point as well as ready solubility is obtained pure with some difficulty. If impure, it decomposes on standing.

Quinone-oxime acetyl ether, $C_6H_4\begin{matrix}=N.O.COCH_3\\ =O\end{matrix}$.—Silver nitroso-phenol, suspended in much absolute ether, reacts quickly on treating with one molecule of freshly distilled acetyl chloride. The etherial filtrate gives a yellow substance in large quantity, which, recrystallised from ligroin (b. pt. 70°–80°), or from a mixture of ligroin and benzene (using animal charcoal), was obtained in light-yellow needles melting at 107°.

0.1898 gram substance, dried over sulphuric acid in a vacuum, gave 0.4046 gram CO_2 and 0.0768 gram H_2O.

0.1864 gram substance gave 14 cc. moist nitrogen at 22° and 750.6 mm.

	Theory for $C_8H_7NO_3$.	Found.
C	58.18	58.14
H	4.28	4.49
N	8.49	8.62

Acetyl-quinone-oxime is but slightly soluble in water; it is odorless, and its etherial and alcoholic solutions are colored green (like those of nitroso-phenol). If dry and finely powdered it causes sneezing.

Quinone-oxime ethyl-carbonic ether, $C_6H_4\begin{matrix}=O\\ =N.O.CO_2.C_2H_5\end{matrix}$.—Equal molecules of chloro-carbonic ether and silver nitroso-phenol, suspended in absolute ether, were heated gently for a short time. The ether extract gives a yellow substance crystallising from ligroin in hexagonal plates melting at 110°. It is identical with an ether obtained by Walker.[1]

0.1208 gram substance, dried over sulphuric acid in a vacuum, gave 0.2456 gram CO_2 and 0.0546 gram H_2O.

0.2616 gram substance gave 16 cc. moist nitrogen at 23° and 752 mm.

	Theory for $C_9H_9NO_4$.	Found.
C	55.38	55.45
H	4.62	5.02
N	7.18	7.08

[1] Ber. d. chem. Ges. **17**, 400.

Quinone-oxime benzoyl ether, $C_6H_4{\overset{O}{\diagup\!\!\diagdown}}N.O.CO.C_6H_5$.—This ether can be obtained in three ways: by treating the dry sodium or silver salt of nitroso-phenol with benzoyl chloride, or by shaking an alkaline solution of nitroso-phenol with benzoyl chloride[1] (best method). The resulting product is purified by repeated crystallisation from alcohol, and obtained thus in light-yellow needles melting at 172°–174°. The alcoholic solutions possess a green color, but not so marked as those of nitroso-phenol or its acetyl ether. This ether is identical with Walker's[2] product, who gives the melting point 168°–175°.

1. 0.2584 gram substance, dried at 100°, gave 13.5 cc. moist nitrogen at 21° and 758 mm. (from Ag salt).

0.1496 gram substance, obtained by Baumann's reaction, gave 0.3752 gram CO_2 and 0.0590 gram H_2O.

2. 0.1996 gram substance, obtained by Baumann's reaction, gave 10.7 cc. moist nitrogen at 20° and 758.3 mm.

	Theory for $C_{13}H_9NO_3$.	Found. I.	II.
C	68.72	68.40	...
H	3.97	4.31	...
N	6.17	6.08	6.26

Quinone-oxime benzyl ether, $C_6H_4{\overset{O}{\diagup\!\!\diagdown}}N.O.CH_2.C_6H_5$.—Silver nitroso-phenol, suspended in absolute ether, is heated for several hours with benzyl chloride (¾ molecule), until the smell of the latter substance has disappeared. The etherial filtrate gives a yellow substance which, recrystallised from ligroin, is obtained in yellow rectangular or rhombic plates melting at 63.5°. The same substance is formed by heating sodic nitroso-phenol in alcoholic solution with benzyl chloride.

0.1514 gram substance, dried over sulphuric acid in a vacuum, gave 0.4068 gram CO_2 and 0.0770 gram H_2O.

0.3300 gram substance gave 19 cc. moist nitrogen at 20° and 762.2 mm.

	Theory for $C_{13}H_{11}NO_2$.	Found.
C	73.24	73.28
H	5.17	5.64
N	6.57	6.60

[1] Ber. d. chem. Ges. **21**, 2744.

[2] Ibid. **17**, 400.

Benzyl quinone-oxime is insoluble in water, but readily soluble in all organic solvents except ligroin. It has no smell. Treated with tin and hydrochloric acid, it is converted into para-amido-phenol, while much benzyl chloride is also formed. The para-amido-phenol obtained was also converted into quinone-chlor-imid (m. p. 84°). This shows that the benzyl group is bound to oxygen, but not in the form of a phenol ether. The conclusive proof that the benzyl ether has the constitution $C_6H_4 \begin{matrix} = O \\ = N.O.CH_2.C_6H_5 \end{matrix}$ is as follows:

The same substance is obtained quantitatively by treating quinone (one gram) dissolved in 250 cc. of water with the calculated amount of *α*-benzyl-hydroxylamine hydrochloride,[1] $C_6H_5.CH_2.O.NH_2$, HCl, dissolved in water containing a few drops of hydrochloric acid. The separation of the ether begins immediately: the reaction is complete in 12 hours, and the product obtained practically pure; yield, 1.95 grams (theoretical, 1.98 grams).

Recrystallised once from ligroin it is obtained in yellow plates melting at 63.5°, and identical in every respect with the above ether obtained from silver or sodium nitroso-phenol.

0.1760 gram substance, dried over sulphuric acid in a vacuum, gave 0.4700 gram CO_2 and 0.0866 gram H_2O.

0.2302 gram substance gave 13 cc. moist nitrogen at 20° and 761.8 mm.

	Theory for $C_{13}H_{11}NO_2$.	Found.
C	73.24	72.84
H	5.17	5.35
N	6.57	6.48

WORCESTER, *April* 19, 1892.

[1] Behrend and Leuchs: Ann. Chem. (Liebig) **257**, 205.

THE COMPOSITION OF THE EXPLOSIVE COPPER AND SILVER COMPOUNDS OF ACETYLENE.[1]

By Edward H. Keiser.

One of the earliest observations made upon the properties of acetylene was that when it is passed into ammoniacal solutions of cuprous chloride and silver chloride, precipitates are formed which after drying are extremely explosive.

As long ago as 1858 Quet[2] observed that when electric sparks are passed through liquid alcohol, a gas is obtained which consists of carbon monoxide and a hydrocarbon. The hydrocarbon gave a brown precipitate with ammoniacal cuprous chloride and a yellow precipitate with ammoniacal silver chloride. He also noticed that these precipitates after being dried are explosive, but he appears to have made no attempts to determine their composition.

Among those who subsequently worked with these compounds were Böttger,[3] Vogel and Reischauer,[4] Torrey[5] and Crova.[6]

Berthelot,[7] however, appears to have been the first to attempt to express the composition of these substances by means of formulas. He concluded from his experiments that they contained radicles consisting of carbon, hydrogen and copper in the one case, and carbon, hydrogen and silver in the other, and that in each case these radicles were in combination with oxygen. Thus the copper precipitate he called *cuprosacetyl oxide*, and gave to i the formula $(C_2Cu_2H)_2O$. The silver precipitate was called *argentacetyl oxide*, and to it was given a similar formula, $(C_2Ag_2H)_2O$.

Other investigators who have studied these compounds have come to different conclusions in regard to their composition. Thus Reboul[8] assigns to the copper precipitate the formula C_2HCu, while for the silver compound he writes the formula $(C_2HAg)_2Ag_2O$. Miasnikoff[9] analysed the silver compound and found that his results agreed best with the formula $C_2H_2Ag_2$. The latest work upon this subject has been done by Blochmann,[10] who analysed

[1] Read at the meeting of the Franklin Institute, Feb. 16, 1892.
[2] Compt. rend. **46**, 903; Ann. Chem. (Liebig) **108**, 116.
[3] Jsb. Chem. 1859, 219. [4] Ibid. 1858, 208. [5] Ibid. 1859, 222. [6] Ibid. 1862, 412.
[7] Ann. Chem. (Liebig) **123**, 216; **138**, 245; **140**, 314.
[8] Ibid. **124**, 267; Compt. rend. **54**, 1227. [9] Ibid. **118**, 330. [10] Ibid. **173**, 176.

both the silver and copper precipitates and concluded that their composition is best represented by the formulas $C_2H_2Cu_2O$ and $C_2H_2Ag_2O$.

These formulas have found their way into the text-books and appear to have been generally accepted. Some authors write the formulas as above, apparently regarding the compounds as made up of molecules of acetylene and of cuprous oxide in the one case, and of acetylene and silver oxide in the other. More recently there seems to be a tendency to regard them as metallic substitution-products of acetylene, and in some of the later works[1] it is stated that perhaps the constitution of these compounds may be represented by some such formulas as:

$$\begin{matrix} C-Ag \\ \| \\ C-Ag \end{matrix} + H_2O \text{ and } \begin{matrix} C-Cu \\ \| \quad | \\ C-Cu \end{matrix} H_2O,$$

or $HC\equiv C-Ag-AgOH$ and $HC\equiv C-Cu-CuOH$.

In view of the uncertainty, therefore, that prevails in regard to the composition of these substances, it seemed desirable to undertake new experiments to determine if possible their true composition, and in anticipation of what follows it may here be stated that it was found as a result of this work that in pure dry condition neither of these bodies contains hydrogen or oxygen, that they are simple carbides of the metals, and that their composition must be represented by the formulas C_2Ag_2 and C_2Cu_2.

Preparation and Analysis of the Silver and Copper Compounds.

In all the experiments the acetylene was made by the action of alcoholic caustic potash upon ethylene bromide. The gas was passed through a second portion of hot alcoholic potash to remove vinyl bromide and was then washed with absolute alcohol. Thereupon the acetylene was passed into the ammoniacal solutions of cuprous chloride, or of silver nitrate. As the copper compound oxidises rapidly in the air, and the silver compound turns black in the light, special precautions had to be taken in washing and drying the precipitates. The washing was carried on in tall cylinders from which the air was removed by a current of carbon dioxide. The precipitates were washed by decantation, first with

[1] Watt's Dictionary, Morley and Muir, **1**, 43; Organische Chemie, V. Meyer and Jacobson, **1**, 456. Ramsay, "Systematic Chemistry," writes the formula of the silver compound HC≡CAg.

water to which ammonia had been added, afterwards with pure water and finally with alcohol and ether. Finally, the precipitates were drained on a funnel by means of the filter-pump, and then quickly transferred to sulphuric acid desiccators which were in connection with a mercury air-pump. The air was then removed and the precipitates allowed to remain until thoroughly dry. The desiccator containing the silver precipitate was protected from the light, and the silver compound when dry was of a snow-white color.

The silver compound was analysed by treating weighed quantities in a porcelain crucible with dilute hydrochloric acid and evaporating to dryness: this was repeated until the weight remained constant. The following results were obtained:

Specimen *A*	0.2588 gram	gave	0.3075 gram	AgCl.
	0.3910 "	"	0.4640 "	AgCl.
Specimen *B*	0.3347 "	"	0.3971 "	AgCl.
Specimen *C*	0.1217 "	"	0.1449 "	AgCl.

	A	*B*	*C*
Percentage Ag—	89.44 89.33	89.31	89.62

Preparations *A* and *B* were dried in a vacuum at ordinary temperatures, while preparation *C* was dried in a vacuum at 100°.

Mean value of silver found = 89.45 per cent.

Berthelot's formula,	$(C_2Ag_2H)_2O$,	requires	86.74 per cent.
Reboul's "	$(C_2AgH)_2Ag_2O$,	"	86.74 " "
Miasnikoff's "	$C_2H_2Ag_2$,	"	89.25 " "
Blochmann's "	$C_2H_2Ag_2O$,	"	83.71 " "
	C_2Ag_2	"	89.99 " "

The percentage of silver found indicates that the formula must be either $C_2H_2Ag_2$ or C_2Ag_2.

To determine whether the compound contains hydrogen, a weighed quantity of the substance was exploded in a vacuum. 0.2225 gram of the substance was placed in a glass tube closed at one end, the open end was filled through a distance of several inches with a long plug of glass-wool and was then connected with a mercury air-pump. After a perfect vacuum had been obtained the substance was gently heated. A bright flash of light indicated that decomposition had taken place. On again exhausting the tube, scarcely any gas at all was obtained; after exhausting the tube for a long time, a volume of gas measuring a cubic centimeter

had collected, but on bringing this gas in contact with caustic potash it nearly all disappeared, showing that it was largely carbon dioxide. If the compound had contained hydrogen, as is indicated by the formula $C_2H_2Ag_2$, it should have given on decomposition about 24 cubic centimeters of gas. The tube containing the decomposed compound was again weighed after the explosion; the weight had remained unchanged. An examination of the black residue left in the tube showed that it consisted of carbon and finely divided silver.

These experiments seem to prove beyond a doubt that the silver compound of acetylene contains only silver and carbon and that its composition is represented by the formula C_2Ag_2.

The copper compound was prepared, washed and dried in the way that has already been described in connection with the silver compound. The percentage of copper in the compound was at first determined by treating a weighed quantity in a crucible with nitric acid and evaporating to dryness, and heating and weighing the copper oxide formed. It was found difficult to obtain accurate results in this way: more or less copper was volatilised although great pains were taken to heat the copper nitrate very gradually. It was found better to dissolve the substance in dilute nitric or hydrochloric acid and to precipitate the copper oxide with caustic soda. By this method the following results were obtained:

Specimen A.

0.3130 gram gave 0.3153 gram CuO = 80.43 per cent. Cu,
0.4085 " " 0.4151 " " = 81.14 " " "

Specimen B.

0.0726 gram gave 0.0735 gram CuO=80.84 per cent. Cu.
0.2120 " " 0.2131 " " =80.27 " " "

Another portion of specimen *B* was dried in a vacuum at a temperature of 100°. 0.2490 gram of the dried compound gave 0.2521 gram CuO=80.90 per cent. Cu. It was noticed that in every case when the copper acetylide was dissolved in acids that small black flakes remained undissolved. An examination of these flakes showed that they consist of carbon. Every specimen of the copper precipitate that was prepared was found to contain some free carbon. The silver compound, on the other hand, was free from carbon. All attempts to prepare the copper acetylide free from carbon

have failed. It appears that when acetylene is conducted into a cuprous solution, and air or oxygen is present in small quantity and the cuprous compound is thereby oxidised to the cupric condition, there is formed the red cuprous acetylide, but at the same time some of the hydrogen of the acetylene or the copper of the precipitate is oxidised and carbon remains behind. For the purpose of obtaining a pure compound other methods of preparation were tried. Acetylene was passed into water in which finely divided cuprous chloride was suspended. There was an abundant formation of the red compound, but this was also found to contain carbon, and it was impossible to remove all cuprous chloride from the precipitate by prolonged washing with ammonia. Acetylene passed into a solution of cuprous oxide in ammonia also gives the red precipitate, but as the cuprous oxide slowly oxidises, the precipitate carries the copper oxide down with it. This specimen contained besides the copper oxide some free carbon. The copper acetylide is so voluminous when first formed that it reminds one of the appearance of ferric and aluminium hydroxides, and like these it carries down small quantities of substances that may be in solution. Owing to the ease with which the moist copper acetylide oxidises in the presence of air, it is extremely difficult to remove these substances by washing.

The purest specimen was obtained by the reaction of acetylene upon cuprous hydroxide suspended in water. The yellow hydroxide is readily converted into the red cuprous acetylide. Even this precipitate contained a trace of carbon. It was analysed by dissolving a weighed quantity in dilute hydrochloric acid. The free carbon was removed by filtration, and in the filtrate the copper, after oxidation, was determined as oxide. The weight of free carbon was deducted from the weight of compound taken.

0.1527 gram gave 0.1593 gram CuO = 83.36 per cent. Cu.
0.0699 " " 0.0735 " " = 83.96 " " "
Berthelot's formula, $(C_2Cu_2H)_2O$, requires 79.3 per cent. Cu.
Blochmann's " $C_2H_2Cu_2O$, " 75.1 " " "
Reboul's " C_2HCu, " 71.7 " " "

The formula C_2Cu_2 requires 84.08 per cent. Cu. The analyses indicate that the formula of the compound is C_2Cu_2. The somewhat lower value of copper obtained is due to the great difficulty of obtaining the compound in pure condition, owing to its tendency to carry down substances that may be in solution. The

presence of a small quantity of copper oxide in the compound would be sufficient to account for the difference noticed.

To determine whether the substance contained hydrogen or water, a weighed quantity of the carefully dried compound was exploded in a vacuum, by the method described under the silver compound. No hydrogen was obtained, nor did the tube change in weight. If water had been present it would have evaporated under the conditions used to bring about decomposition, and its weight could have been determined by the loss in weight of the tube.

The conclusions reached as a result of these experiments are that the composition of the copper and silver compounds of acetylene is best represented by the formulas

$$C_2Cu_2 \text{ and } C_2Ag_2.$$

The silver compound can readily be obtained in pure condition by the process of preparation described above. The copper compound, on the other hand, is nearly always impure; it contains free carbon, and owing to its colloidal nature carries down both cuprous and cupric salts which may be present.

The hydrogen of acetylene is evidently of an acid character and replaceable by metals. Berthelot has shown that when sodium and potassium are heated in a current of acetylene, the compounds C_2Na_2 and C_2K_2 are formed; and indeed it was by the decomposition of the latter substance, obtained in the preparation of metallic potassium, that E. Davy in 1836 first obtained the hydrocarbon. While the acetylene derivatives of the alkali metals can thus be obtained at high temperatures in the absence of water, those of the metals that do not decompose water can be readily formed at ordinary temperatures and in the presence of water. Thus the cuprous and silver derivatives are formed by the direct action of acetylene upon aqueous or ammoniacal solutions of cuprous and silver salts.[1] Mercury and gold compounds have also been obtained, and it seems probable that these are of analogous composition.

[1] Acetylene passed into a concentrated aqueous solution of silver nitrate gives a white precipitate which is much more explosive than the compound prepared from an ammoniacal solution. It has the composition represented by the formula $C_2Ag_2.AgNO_3$.

	Calculated for $C_2Ag_2.AgNO_3$.	Found.
Ag	79.02	79.06

With dilute aqueous solution of silver nitrate C_2Ag_2 is formed. With ammoniacal silver chloride solution C_2Ag_2 is precipitated.

When finely divided metallic copper, obtained by precipitation, is suspended in water and acetylene passed through, the copper is partially converted into C_2Cu_2.

MENTHENE.

By F. A. Sieker and Edward Kremers.

In a recent number of the "Berichte"[1] Brühl states that menthene can be obtained by the dehydration of menthol with anhydrous copper sulphate. A year ago one of us[2] reported on some oximes obtained from pennyroyal oil, and mentioned incidentally that dehydration experiments with menthone were being conducted. The investigation had to be interrupted, and since the anticipations were not realised, the dehydration of menthol was taken up in preference. This has been effected in various ways since Walter in 1838 first prepared menthene by the action of glacial phosphoric acid upon menthol. The dehydrating agents, phosphoric acid anhydride, zinc chloride, sulphuric acid, etc., however, not only effect the hydration of menthol, but also destroy in part the desired hydrocarbon, as becomes quite evident from the large percentage of by-products resulting. Since potassium acid sulphate has been of such admirable service in the dehydration of terpineol and terpin, it was tried and soon proved to be very satisfactory. After this fact had been established and while we were trying to make the nitrosite and nitrosyl-chloride addition-products of the hydrocarbon, Brühl's report came to our notice. We, therefore, feel constrained to make this preliminary report.

To prepare menthene, 50 grams of menthol and 100 grams of potassium acid sulphate are heated in a strong flask connected with a reflux condenser on a paraffin-bath for 6–8 hours at a temperature of from 180°–200°. The mixture is then distilled with water-vapor and the oily distillate is dried with the aid of caustic potassa. After repeated careful fractionation the oil was resolved chiefly into menthene, boiling at 167°–168°, and unchanged menthol. The by-products are altogether insignificant. The menthene thus obtained is a colorless, mobile liquid of a peculiar (*not menthol-like*) odor. Its specific gravity at 20° was found to be 0.814. It is strongly *dextro-gyratory*, whereas the menthol from which it is obtained is laevo-gyratory: $[\alpha]_D = +26\ 40°$.[3]

[1] "Untersuchungen über die Terpene und deren Abkömmlinge," Ber. d. chem. Ges. **25**, 142.

[2] Pharm. Rundschau, 1891, p. 131.

[3] The higher fractions have a somewhat higher specific gravity, but are optically less active, thus indicating the presence of unchanged menthol. More careful determinations of the physical constants have been recently made by Mr. Urban.

Upon combustion it yielded the following results:

0.1664 gram substance gave 0.5250 gram CO_2=0.14318 gram C; and 0.1966 gram H_2O=0.02184 gram H.

	Calculated for $C_{10}H_{18}$.	Found.
C	86.95	86.04
H	13.04	13.12

As already mentioned, the investigations of menthene heretofore were more or less unsatisfactory because no crystalline derivatives were obtained. Since the nitrosites, nitrosates and nitroso-chlorides of the terpenes were found to be of such value in the isolation and investigation of the terpenes, the attempt was made to prepare one of these compounds from menthene. The nitrosite reaction as applied to terpinene by Wallach was not successful. The nitroso-chloride reaction, however, proved to be a success. 15 cc. of menthene were dissolved in 15 cc. of glacial acetic acid and 11 cc. of ethyl nitrite, and the solution kept cold in a freezing-mixture. To it 6 cc. of hydrochloric acid, previously dissolved in an equal volume of glacial acetic acid, were added gradually. A white crystalline precipitate was formed, and was separated by filtration and dried on porous plate. 15 grams of menthene yielded about 4 grams of nitroso-chloride. The nitroso-chloride was purified by dissolving it in the smallest possible quantity of chloroform, filtering the solution and precipitating with alcohol.

The nitroso-chloride thus purified is a white crystalline powder, that showed no signs of decomposition even after three weeks. It melts at 113° *without decomposition*, but decomposes, as shown by the evolution of gases, at about 152°. It is altogether remarkable for its stability. Even in contact with the acid mother-liquid it shows no signs of decomposition after several days when kept cold. It is readily soluble in chloroform, not quite as soluble in ether, and but sparingly soluble in alcohol.

Upon analysis it yielded the following results:

I. 0.1920 gram substance gave 0.4101 gram CO_2=0.11184 gram C; and 0.1589 gram H_2O=0.01765 gram H.

II. 0.1998 gram substance gave 12 cc. N at 17° under pressure of 746 mm.=0.0136737 gram N.

III. 0.2004 gram substance gave 0.1305 gram AgCl=0.03227 gram Cl.

Calculated for $C_{10}H_{18}NOCl$.		Found. I.	II.	III.
C	58.99	58.24	...	...
H	8.84	9.19	...	...
N	6.88	...	6.84	...
Cl	17.40	...	...	16.10

By heating menthene nitroso-chloride with an alcoholic solution of benzyl-amine a crystalline substance was obtained which very likely is a nitrol-amine base.

Menthene being a derivative of tetrahydro-benzene, its first crystallisable derivative must be of considerable interest, especially as this must, no doubt, lead to many more. A study of these derivatives must also throw more light upon the analogous derivatives of the terpenes. The disputed question whether menthene occurs in oil of peppermint or not can now be answered; the identity of dihydro-dipentene ("Dihydrocynen") with menthene also can be established or denied. By splitting off hydrogen chloride from the nitroso-chloride, dihydro-carvoximes may be expected to result, etc., etc. The study of menthene, of its nitroso-chloride and other derivatives, will be continued.

PHARMACEUTICAL LABORATORY, UNIVERSITY OF WISCONSIN, *April* 20, 1892.

Contributions from the Chemical Laboratory of Wesleyan University.

X.—ON THE ACTION OF ACETYL CHLORIDE ON ORTHO-HYDROXY-ALDEHYDES.

BY W. P. BRADLEY AND F. B. DAINS.

Nearly three years ago an advance paper was published by one of the writers[1] describing the first results of an investigation of disalicylic aldehyde. The present paper is in continuation of the same work, which was for some time unavoidably interrupted.

Disalicylic aldehyde, $C_{14}H_{10}O_3$, was first obtained by Ettling[2] as a product of the dry distillation of the copper salt of salicylic aldehyde. In 1851 Cahours[3] obtained it, strangely enough, by the action of benzoyl chloride on salicylic aldehyde. Later investi-

[1] Ber. d. chem. Ges. **22**, 1134. See also W. P. Bradley: Inaug. Diss., Göttingen, 1890.
[2] Ann. Chem. (Liebig) **35**, 255; **53**, 77. [3] Ibid. **78**, 228.

gations[1] have shown that acid chlorides in general convert free salicylic aldehyde into this condensation-product. The effect of their action is therefore the extraction of one molecule of water from two molecules of the aldehyde, which may be represented by the formula:

$$2C_7H_6O_2 = C_{14}H_{10}O_3 + H_2O.$$

So far as is known, no other dehydrating agents produce this compound.

Disalicylic aldehyde possesses none of the properties of aldehydes or phenols. Ordinary oxidising agents do not affect it, nor can it be reduced. It unites neither with phenyl-hydrazine nor with hydroxyl-amine. It is insoluble in alkalies and is not affected even by melted potassium hydrate. Certain acid reagents, however, reconvert it into salicylic aldehyde or derivatives of it. Thus, a quantitative yield of salicylic aldehyde is obtained by the action of concentrated sulphuric acid at the ordinary temperature. Fuming hydrochloric acid at 120°–130° produces the same result, but incompletely. Bromine dissolved in glacial acetic acid yields a mixture of monobrom and dibrom-salicylic aldehyde, para-dibrom-disalicylic aldehyde, $C_{14}H_8Br_2O_3$, and considerable quantities of unchanged disalicylic aldehyde. Nitric acid of sp. gr. 1.44, when boiled with powdered disalicylic aldehyde, produces a dinitro-salicylic acid.

Until the present portion of the work of investigating disalicylic aldehyde was commenced, but a single derivative of the compound was known, viz. the dibrom-derivative mentioned above. From the mixed product resulting from the action of bromine upon disalicylic aldehyde, the monobrom and dibrom-salicylic aldehydes, being soluble in alkali, were easily removed; but all attempts to separate the unchanged disalicylic aldehyde completely from its dibrom-derivative failed. Although a pure compound could not be obtained in this way, it was found that the same method used to produce disalicylic aldehyde from salicylic aldehyde could be employed to convert monobrom-salicylic aldehyde into dibrom-disalicylic aldehyde. The large yield obtained could easily be separated from any unchanged brom-salicylic aldehyde by the use of alkali, in which of course the latter is soluble. It seemed, therefore, probable that this peculiar reaction of acetyl chloride might prove to be of general application to all aldehydes having

[1] Ann. Chem. (Liebig) **145**, 299; Suppl. **8**, 42; **244**, 46.

an hydroxyl group in the ortho position. With the object in view of testing the truth of this conclusion, the following ortho-hydroxy-aldehydes have thus far been studied.

Para-chlor-salicylic aldehyde.—Para-chlor-salicylic aldehyde[1] (m. p. 99.5°) was prepared by leading a stream of dry chlorine gas into salicylic aldehyde dissolved in glacial acetic acid. The solution turns yellow, becomes warm, and if not too dilute, deposits crystals of chlor-salicylic aldehyde. A small amount of dichlor-salicylic aldehyde forms at the same time. In order to bring about condensation, the former was subjected in the main to the same treatment which had been found successful in the case of the analogous monobrom-salicylic aldehyde. A small excess of glacial acetic acid was employed as a solvent, and an amount of acetyl chloride was added equal in weight to half the chlor-salicylic aldehyde employed. Reaction begins at once with evolution of considerable heat. After standing several hours the mixture is heated on the water-bath to complete the reaction, and then poured into water. Dichlor-disalicylic aldehyde together with some unchanged monochlor-salicylic aldehyde is precipitated in solid form, and may be obtained free from the latter by washing with dilute alkali. It will be well to state that as a rule it is not advisable to increase the relative amount of acetyl chloride employed beyond what is indicated above. In some cases, notably that of para-methyl-salicylic aldehyde, to be described later, such an increase leads to the formation of large quantities of a gummy substance, difficult or impossible to work.

The yield of dichlor-disalicylic aldehyde averages about 60–70 per cent. of the theoretical. This compound does not crystallise notably well from any solvent yet tried. From a hot concentrated solution in alcohol it may be obtained in fine white silky needles. Out of more dilute solutions it crystallises in very long slender filaments, which fill the entire liquid as with a kind of moss or mould. In either case the crystals melt at 172°.

Analysis.—0.1902 gram compound gave 0.1874 gram AgCl (Carius).

	Found.	Calculated for $C_{14}H_8Cl_2O_2$.
Cl	24.27	24.03

Dichlor-disalicylic aldehyde is quite easily soluble in alcohol, ether, acetic acid, benzene, chloroform, and carbon bisulphide, less

[1] Ann. Chem. (Liebig) **30**, 171; Berzelius' Jsb. **20**, 311.

soluble in petroleum ether. Like disalicylic aldehyde itself, it is easily soluble in concentrated sulphuric acid, and the resulting amber-colored liquid, when poured into water, deposits quantitatively para-chlor-salicylic aldehyde.

Dibrom-dichlor-salicylic aldehyde.—Dibrom-salicylic aldehyde[1] (m. p. 82.5°), whether treated with acetyl chloride in the usual way, or in a sealed tube at 115°–130° C., gave no traces of any condensation-product, but was recovered unchanged. Similarly with dichlor-salicylic aldehyde no condensation could be effected, as far as our experiments with it extended.

Para-nitro-salicylic aldehyde.—Para-nitro-salicylic aldehyde[2] was dissolved in glacial acetic acid and half its weight of acetyl chloride was added. There was no rise of temperature, and no condensation took place. In subjecting the mixture, however, to a temperature of a 100° C. in a sealed tube, a very small quantity of a substance was obtained which was insoluble in alkali, and which was deposited from its solution in ether in small yellow crystals melting at about 220° C. All efforts to secure in this manner enough of the substance to purify and analyse proved fruitless, and yet, in view of what follows, it can hardly be questioned that we were dealing with para-dinitro-disalicylic aldehyde. We were in fact able to obtain the latter by a direct nitrification of disalicylic aldehyde itself; for while boiling nitric acid of 75 per cent.[3] by cleavage, oxidation, and nitrification produces at once nitro-derivatives of salicylic acid, it was discovered that fuming acid at 0° C. effected simply the introduction of nitro groups into the molecule of disalicylic aldehyde.

Into successive portions of fuming nitric acid of about 20–25 cc. each, well cooled in ice-water, finely powdered disalicylic aldehyde was dropped in small quantities and agitated as long as it dissolved easily. All rise of temperature must be carefully avoided, in order to prevent the formation of considerable quantities of a glue-like substance which seriously interferes with the subsequent crystallisation and purification of the nitro-products formed. When the operation is ended the red liquid is allowed to remain about fifteen minutes at 0° and is then poured into a large quantity of ice-water. The solid precipitate which forms is washed thoroughly with dilute alkali and with water. It is composed mainly

[1] Ann. der Phys. Pogg. **46**, 71; Berzelius' Jsb. **25**, 486; Bull. Soc. chim. (Paris) **46**, 277; and Inaug. Diss., p. 30.

[2] Ber. d. chem. Ges. **20**, 1928.

[3] Inaug. Diss., 29.

of para-dinitro-disalicylic aldehyde, with a probable admixture of mononitro and trinitro compounds,—possibly, also, of isomeric dinitro-derivatives. Great difficulty was encountered in the separation of the individual components. After a long and wearisome process of fractional crystallisation out of acetic acid and benzene, —these solvents having been found to give most satisfactory results—the greater portion of the yield was obtained in the form of small, compact, strongly refracting crystals, of a pale yellow color, and melting at 221° when pure.

Analysis.—I. 0.4239 gram substance gave 0.1025 gram H_2O and 0.8254 gram CO_2.

II. 0.2614 gram substance gave 20.2 cc. N measured at 759 mm. of mercury and 11.5° C.

	I.	II.	Calculated for $C_{14}H_6(NO_2)_2O_3$.
C	53.10	...	53.17
H	2.68	...	2.53
N	...	9.18	8.86

Para-dinitro-disalicylic aldehyde dissolves with difficulty in alcohol, acetic acid, ether, chloroform, carbon bisulphide, and petroleum ether, and but little more freely in benzene. The striking similarity in every respect between this compound and that obtained from para-nitro-salicylic aldehyde by means of acetyl chloride, left little doubt as regards the position of the nitro groups in it. Direct proof was furnished by the action of concentrated sulphuric acid upon the compound. Solution was easily effected with the aid of gentle heat, and the addition of water to the red liquid precipitated quantitatively para-nitro-salicylic aldehyde, melting at 126°.

Out of the same mixture of nitro-products from which para-dinitro-disalicylic aldehyde was isolated, at least two other fractions were obtained, which showed fairly constant melting-points of about 180° and 250° respectively. The conclusion was easy that these contained respectively a mononitro and a trinitro-derivative of disalicylic aldehyde; but as neither of the fractions could be obtained in quantities large enough to admit of the necessary purification, no proof of its correctness could be furnished.

Ortho-nitro-salicylic aldehyde.[1]—Ortho-nitro-salicylic aldehyde (m. p. 109°) appears to be wholly unaffected by acetyl chloride, both at ordinary temperatures and in a sealed tube. No conden-

[1] Ber. d. chem. Ges. **20**, 1928.

sation-product was obtained in this way, nor could any ortho-dinitro-disalicylic aldehyde be obtained by the direct nitrification of disalicylic aldehyde.

α-Aldehydo-β-naphthol.[1]—This compound, obtained by Kauffmann by the action of chloroform and potassium hydroxide upon β-naphthol, condenses very easily indeed by the use of acetyl chloride. The reaction is accompanied by evolution of heat and the deposition of a part of the condensation-product sought in crystalline form. The total yield is nearly quantitative. For purposes of purification, acetic acid or benzene may be employed as solvents. After one or two crystallisations, the product, β-diortho-oxy-α-naphthaldehyde, is found to be sufficiently pure for analysis.

Analysis.—I. 0.3386 gram substance gave 0.1324 gram H_2O and 1.0018 grams CO_2.

II. 0.3358 gram substance gave 0.1294 gram H_2O and 0.9928 gram CO_2.

III. 0.3102 gram substance gave 0.1199 gram H_2O and 0.9154 gram CO_2.

	Found.			Calculated for
	I.	II.	III.	$C_{22}H_{14}O_2$.
C	80.56	80.65	80.48	80.98
H	4.19	4.29	4.29	4.30

The compound dissolves with difficulty in the ordinary solvents. From benzene or acetic acid it is deposited in small, hard, nearly white crystals, melting at 241° C., which soon acquire a tinge of red. Concentrated sulphuric acid dissolves it, as it does all the condensation-products of this class so far investigated. The solution is of a dark-red color, with a green fluorescence, and when diluted with water deposits α-aldehydo-β-naphthol.

Para-methyl-salicylic aldehyde.[2]—The method here employed with ortho-oxy-aldehydes gave with para-methyl-salicylic aldehyde a nearly quantitative yield of para-dimethyl-disalicylic aldehyde. After washing the latter thoroughly with dilute alkali it was found to contain traces of chlorine when heated upon a piece of copper oxide in the colorless Bunsen flame. After repeated crystallisations the halogen still remained. It was found advisable, therefore, to boil the crude condensation-product with a concentrated solution of alkali for 15–20 minutes, after which it showed no trace of halogen and was easily purified by recrystallisation. In a state of purity it melts at 141° C.

[1] Ber. d. chem. Ges. **15**, 805. [2] Ibid. **11**, 773.

Analysis.—0.2172 gram substance gave 0.1086 gram H_2O and 0.5997 gram CO_2.

	Found.	Calculated for $C_{16}H_{14}O_3$.
C	75.30	75.60
H	5.51	5.56

Although para-dimethyl-disalicylic aldehyde is not readily soluble in acetic acid, it is sufficiently so to allow of a determination of its molecular weight by the method of Raoult. 74.25 grams of glacial acetic acid were used as a solvent. A depression in the freezing point amounting to 0.046° was obtained by the solution of 0.1797 gram of the substance under discussion. This corresponds to a molecular weight of 251.2. The calculated value is 254.

The compound is quite easily soluble in most solvents. Petroleum ether dissolves it with difficulty and deposits it in beautiful oblong tables pointed at either end. Para-dimethyl-disalicylic aldehyde differs from the derivatives thus far mentioned in being easily volatile with steam, although considerably less so than disalicylic aldehyde itself. Concentrated sulphuric acid reconverts it into para-methyl-salicylic aldehyde.

Efforts to oxidise one or both methyl groups to carboxyl have thus far failed. Protracted boiling with even a 15-per cent. alkaline solution of permanganate produced no effect.

Ortho-aldehydo-salicylic acid.—This compound, prepared according to directions given by Reimer and Tiemann,[1] is not condensed in the slightest degree by acetyl chloride, even when a mixture of the two is heated in a sealed tube to 150° C.

The ultimate object of the general investigation of which the above is a part, is the determination of the constitution of disalicylic aldehyde, for which a provisional formula has already[2] been proposed. Work along these and cognate lines will be continued. Among the compounds whose conduct is to be studied are aldehydo-derivatives of ortho- and meta-kresol, of resorcin and pyrocatechin or their ethers; ortho-hydroxy-ketones; and hydroxy-aldehydes and ketones of the methane series. As regards the special question whose answer was sought in the foregoing experiments, it is obviously too early as yet to draw definite conclusions. It appears probable, however, that acetyl chloride is able to secure quantitative condensation of all ortho-hydroxy-aldehydes in which

[1] Ber. d. chem. Ges. **9**, 1272; **10**, 1564. [2] Inaug. Diss., p. 37.

only hydrocarbon groups are joined directly to the benzene ring. The introduction of negative groups hinders or entirely prevents condensation. Thus the presence in the molecule of a single chlorine or bromine atom diminishes the yield 30–40 per cent. The presence of a single nitro group in the para position nearly prevents condensation. A nitro group or a carboxyl in the ortho position, or the presence of two halogen atoms, prevents it altogether.

A NEW COLOR-STANDARD FOR NATURAL WATERS.

By Allen Hazen.

After the disease-producing qualities, which we may believe are mainly dependent upon living germs, there is no subject connected with the examination of potable waters which deserves more careful consideration than their physical characteristics. The public very properly desire that the water which they drink shall not only be of such purity that it will not cause diarrhea, typhoid fever or other disease, but also that it shall be free from offensive tastes, odors and appearance. It is well known that these physical characteristics bear no definite relation to the power of causing serious disease; that dirty and discolored waters may nevertheless be not unwholesome, while in some cases a beautifully clear water may carry the germs of typhoid fever; and it is not with any intention of determining the wholesomeness of waters that we undertake the study of their colors. We wish to know how various water supplies compare in color; what changes take place in the same supply at different seasons of the year, and what treatments and conditions remove or tend to remove color. In order to obtain this information we require a standard by which to measure accurately the colors in question,—a standard which shall be the same at all times in the same laboratory, and that can be conveniently prepared by different chemists so as to yield strictly comparable results.

Standards now in Use.

As early as 1878[1] Prof. A. R. Leeds suggested the use of nesslerised ammonia as a standard of color. The color of a water was recorded as the number of cc. of an ammonia solution, 0.01 mg. NH_3 per cc., which when mixed with 50 cc. of distilled water and nesslerised would produce an equal color. The great advantages of this process were the ease and simplicity of the determination, as the necessary apparatus and standards were always present in laboratories for water analysis, being required for another purpose; and also that the figures were supposed to have a definite value based on the amount of ammonia used. The objections to its use, as will be shown, are that the colors depend upon temperature, and upon the composition and amount of the Nessler reagent used, and upon other details of manipulation to such an extent as to make uncertain the exact value of the results, and also that the figures obtained are not proportional to the coloring matter present.

The use of highly colored natural waters for standards, the colors of which are checked by comparison with nesslerised ammonia, and which are diluted for use as required, as suggested by Mrs. Richards,[2] overcomes some of the objections to the nesslerised ammonia standard, but at the same time makes the process somewhat arbitrary.

In 1881 Messrs. Crookes, Odling and Tidy[3] described an instrument for measuring the colors of waters. It consisted of a pair of 2-ft. tubes, one of which contained the water under examination, while the other remained empty. Behind the empty tube were placed two hollow wedges, one containing a 1-per cent. copper sulphate solution, the other a solution of ferric and cobalt chlorides containing 0.7 gram iron and 0.3 gram cobalt per liter, with "a very slight excess of free hydrochloric acid." These wedges were pushed over the empty tube until their color matched that of the water in the other tube, and the color was recorded as equal to so many millimeters of blue and of brown solutions. With this apparatus the colors of the various water-supplies of London have been measured up to the present time. The fatal objection to this process is that the color of the brown solution is affected by the amount of free hydrochloric acid, and by temperature, to such an extent that it is totally unfit for a general standard.

[1] Proc. Am. Chem. Soc. **2**.
[2] Rep. Mass. State Board of Health, Examination of Water Supplies, 1890, p. 532.
[3] Chem. News. **43**, 174.

Platinum Color-Standard.

The objections to the nesslerised ammonia standard may be avoided in another way, while still retaining its simplicity, by the use of colored metallic solutions of definite composition. The use of iron for this purpose is inadmissible, as has been said, because its color depends in a controlling degree upon acidity and temperature, but the colors of several other metallic salts are quite independent of these conditions, and may therefore be used. A mixture of the chlorides of platinum and cobalt leaves little to be desired. The color of such a solution is, within wide limits at least, entirely independent of acidity and temperature, and when mixed with a moderate amount of hydrochloric acid, it is quite stable even in direct sunlight.

By varying the ratio of cobalt to platinum, the hue of any clear natural water, when not seen in too great depth, can be perfectly matched; but for all practical purposes, a single solution containing one-half as much cobalt as platinum is sufficient. Some waters will appear slightly redder than this; some slightly greener; but the differences are very much less than those between waters and nesslerised ammonia, and are quite unimportant.

We can conveniently express the color of a water in terms of the amount of platinum required to produce an equal color, and we have: *The color of a water is the amount of platinum, in parts per ten thousand, which, in acid solution, with so much cobalt as will match the hue, produces an equal color in distilled water.* I suggest that this be called the *platinum color-standard.*

Method of Application.—To make the standards, a solution having a color of 5. is a convenient starting-point. This can be made by dissolving 1.246 grams potassium-platinum chloride, containing 0.5 gram platinum, and 1 gram crystallised cobalt chloride, free from iron, containing 0.25 gram cobalt, in water with 100 cc. concentrated hydrochloric acid, and making up to one liter. A solution so prepared has remained unaltered for one year, although exposed to the light, and at times to direct sunlight. Standards for use are made by diluting 1, 2, 3 cc. etc., of this solution to 50 cc. in Nessler tubes, giving colors 0.1, 0.2, 0.3, etc. In clean tubes, and protected from dust when not in use, they will keep for months, and can be replaced at any time from the strong solution.

If the standards made as above do not perfectly match waters having hues different from those with which we are familiar, more

or less cobalt may be used, keeping the platinum, which is the real standard, always the same.

Long Tubes for Low Colors.—Colors can be read as described above in 200-mm. Nessler tubes with ample accuracy for all ordinary purposes; but for some experimental work with clear light-colored waters, where the greatest possible accuracy was desired, 600-mm. tubes have been found more satisfactory. We have used a pair of brass tubes closed with plate-glass ends, from which the luster of the brass inside was removed by a dilute solution of sugar of lead. One tube is filled with distilled water, the other with the water under examination. The tubes, held by a suitable support, are pointed at a piece of ground glass in a window, with a slight angle between themselves so that the contents of both tubes can be seen from a little distance with one eye. If the two tubes look alike, the water is colorless; that is, it contains no foreign coloring matter. If the water is yellow, it is matched by placing a flat-sided jar of platinum cobalt solution behind the distilled water. The jars, of which there are a series corresponding to colors 0.01, 0.02, 0.03, etc., contain standard solutions as many times as strong as would be used for direct comparison, as the 600-mm. tube of water is longer than the thickness of the solutions in the jars.

The results so obtained are directly comparable with readings in Nessler tubes in the case of clear waters with colors of 0.3 or less, and the probable error is very much less. With turbid waters, however, the results in the long tubes are higher, the difference increasing with the turbidity.

Instead of using a single set of jars, each containing both platinum and cobalt, two sets can be used—one of platinum and one of cobalt. In this way the hues of different waters, and particularly those of turbid waters, can be more accurately matched, and also, if desired, a record can be made in each case of the ratio of cobalt to platinum required. This method is considerably more laborious than when the two metals are combined in a single solution, and the results obtained very rarely differ to an appreciable extent.

Limit to the Length of Tube.—The 600-mm. tubes should not be used for water having more than a very slight turbidity, or for colors above 0.3, as in such cases a more accurate comparison can be made in a less depth of liquid. In the same way, with very

highly colored waters, the best results are obtained with columns of liquid shorter even than a 200-mm. Nessler tube, and, in a general way, it may be said that the product of the color and the depth of water used for comparison in millimeters should not exceed 180. Thus colors above 0.3 should not be read in 600-mm. tubes; above 0.9, in 200-mm. tubes; above 1.8, in 100-mm. tubes, etc. This is particularly important when only a single ratio of cobalt to platinum is used; for with the same water in great depth, more cobalt is required in proportion to the platinum than in a less depth. Up to the limit given these variations are quite unimportant, and do not in any way affect the results; but with deeper colors the variations increase far more rapidly than the increase in color, and may seriously vitiate the results if tubes are used considerably longer than the above limits. Instead of using very short tubes for extremely high colors, good results can be obtained by diluting the water five or ten times with distilled water, and calculating the original color from the measured color of the dilution.

The Nesslerised-Ammonia Standard.

We have at the present time the records of many thousand water analyses in which the colors have been determined by comparison with the nesslerised-ammonia standards. In fact, it might almost be said that all our knowledge of the colors of American waters is expressed in terms of this unit. It is, therefore, of prime importance to inquire how the proposed standard compares with that most generally in use.

Some Considerations in regard to Nesslerisation.—The colors produced by nesslerising ammonia depend upon temperature, and upon the quality and quantity of Nessler reagent, and upon whether the ammonia is mixed with the water before nesslerisation or not. The Nessler solution used for the following experiments, except when otherwise stated, was made by dissolving 70 grams potassium iodide in a little water, adding cold saturated solution of mercuric chloride to slight permanent pink, then 500 cc. of a solution of potassium hydrate (500 grams per liter), and 10 cc. more mercuric chloride. Water is added to make 2 liters, and it is allowed to stand some days before use. The ammonia-free water used for making the standards was prepared by blowing steam through ordinary good distilled water, and contained, as found by dis-

tillation, 0.0002 to 0.0004 part per 100,000 ammonia. The standard ammonia solution, containing 0.01 mg. ammonia per cc., was thoroughly mixed with this water before nesslerising with 2 cc. of reagent, at temperatures ranging only from 18° to 21°. The colors produced at the end of half an hour were measured by the platinum color standard as described above, except that no cobalt was required to match the lower Nessler standards, as they have much less red than natural waters.

Quantity of Nessler Reagent used.—The following table shows the colors produced by nesslerising different amounts of ammonia with 0.5, 1, 1.5, 2, 2.5, and 4 cc. of Nessler reagent:

Nessler reagent used,	0.5	1.0	1.5	2.0	2.5	4.0
Ammonia solution, 0	.05	.07	.10	.14	.17	.25
0.1 cc.	.05	.07	.10	.16	.22	.37
0.2	.05	.07	.18	.30	.37	.45
0.3	.05	.15	.37	.43	.45	.55
0.5	.13	.45	.55	.60	.62	.65
1.0	.65	.90	1.00	1.05	1.10	1.15
2.0	1.30	1.80	1.90	2.00	2.00	2.00
4.0	3.80	4.50	5.00	5.00	5.00	5.00

With the lower standards the colors depend quite as much upon the quantity of Nessler reagent as upon the quantity of ammonia. Thus the 0.2 standard with 1.5 cc. reagent, the 0.1 standard with 2 cc., and distilled water with 2.5 cc. give substantially equal colors. With the higher standards the quantity of reagent is of less consequence. An interesting point is that a certain amount of reagent is required to produce any color with the low standards; 0.5 cc. reagent produces no color whatever, that is, no more than its own color in distilled water, when added to the 0.3 standard; 1 cc. reagent does not bring out the 0.2 standard; and 2 cc., the usual quantity, hardly affects the 0.1 standard, 2.5 cc. being required to show a distinct increase in color.

When a set of standards is made from water absolutely free from ammonia and with the usual Nessler reagent, there will be hardly any color in the 0.1 standard above that of the nesslerised distilled water; the higher standards will increase regularly in color. If, however, instead of strictly ammonia-free water, a water containing 0.0010 or 0.0020 ammonia is used, and such a water would be considered "ammonia-free" if not tested by distillation,

the blank shows only the color of the Nessler reagent, while the 0.1 and succeeding standards show a regular and marked increase in depth. Such a set of standards is apparently more satisfactory than those made from strictly ammonia-free water, but will obviously give quite different color results. The 0.1 standard can be brought out by using either more or stronger Nessler reagent; but if this is done, all the colors will differ from those obtained under the usual conditions.

Quality of Nessler Reagent.—Different samples of Nessler reagent differ considerably in the colors which they produce with the lower standards, even when made by the same formula.

Other conditions being the same, the amount of color produced with the lower standards increases with the alkali in the reagent used. Three lots of Nessler solution were made side by side and in precisely the same way, except that the amount of caustic potash was varied, the three portions containing 50, 125, and 200 grams per liter respectively. The colors produced by nesslerising ammonia with 2 cc. of these solutions were as follows:

Quantity of alkali in Nessler reagent:

Ammonia Solution.	50 grams KOH.	125 grams KOH.	200 grams KOH.
0	.22	.14	.15
0.1 cc.	.22	.16	.20
0.2	.25	.37	.40
0.3	.30	.45	.50
0.5	.40	.62	.65
1.0	.90	1.05	1.05

The colors also depend upon the amount of potassium iodide and mercuric chloride present. Three lots of Nessler solution were prepared containing respectively 20, 35, and 50 grams potassium iodide per liter, with corresponding amounts of mercuric chloride, the alkali being 125 grams in each case. The colors produced were as follows:

Quantity of iodide in Nessler reagent:

Ammonia Solution.	20 grams KI.	35 grams KI.	50 grams KI.
0	.13	.14	.25
0.1 cc.	.13	.16	.37
0.2	.13	.37	.50
0.3	.30	.45	.58
0.5	.55	.62	.70
1.0	1.05	1.05	1.10

When both alkali and iodide vary, the result is the same as with varying amounts of the same solution; 2 cc. of a dilute reagent give the same result as 1 cc. of twice as concentrated a solution.

Mixing.—With the standards 0.1 and 0.2 a much higher color than is otherwise obtained is produced when the ammonia is added to the distilled water in the tube and is immediately nesslerised before it becomes mixed with the water. With the standards 0.3 and above, no corresponding differences are observed. The average results obtained are as follows:

Effect of mixing:

Ammonia Solution.	Mixed.	Not Mixed.
0	.14	.14
0.1 cc.	.16	.26
0.2	.30	.37
0.3	.43	.45
0.4	.52	.52

Temperature.—The color produced by nesslerising ammonia also depends upon temperature;[1] the higher the temperature the darker and redder is the color produced, but with the lower standards the errors introduced by variations of not more than two or three degrees are comparatively small.

Bearing upon Ammonia Determinations.—It will be observed that the above-mentioned sources of error in the measurement of colors have no direct bearing upon the accuracy of ammonia determinations when properly carried out. There, the absolute amount of color is of no consequence; it is only important that under the same conditions equal quantities of ammonia yield equal colors. The results suggest, however, the necessity of accurately measuring the Nessler reagent used, especially for the lower standards, and of having strictly ammonia-free water and a sufficiently concentrated and sensitive Nessler reagent to strike colors with the lowest standards.

Comparison of the Platinum and Nesslerised-ammonia Standards.

It can hardly be expected, in view of the above observations, that the same results will be obtained with the nesslerised-ammonia standard in different laboratories. It would seem inevitable, in the absence of a rigorous definition of the details of manipulation, that different workers should obtain different results. In

[1] This Journal **19**, 425.

giving the following figures, which are the average of a large number of trials made under the conditions indicated above, I am fully aware that they represent the nesslerised-ammonia standard only as it has been used in this laboratory, and that great caution must be used in applying them to results obtained by that process elsewhere.

Nesslerised Ammonia.	Platinum.	Nesslerised Ammonia.	Platinum.
0	0.14	0.7	0.78
0.1	0.16	0.8	0.87
0.2	0.30	0.9	0.96
0.3	0.43	1.0	1.05
0.4	0.52	1.5	1.50
0.5	0.60	2.0	2.00
0.6	0.69	3.0	2.80

These figures bring out some interesting facts. The nesslerised-ammonia standard has no place for colors which match less than 0.14 platinum. All that can be done with waters having colors below 0.1 and yet having definite colors, is to record them as 0.05—an arbitrary proceeding, since the color is by no means equal to that obtained by nesslerising 0.05 cc. ammonia solution in 50 cc. distilled water. With the nesslerised-ammonia standard the figures obtained are not proportional to the color: color 0.5 is only twice as deep as color 0.2; color 0.8 is only twice as deep as color 0.3; color 1.0 is only twice as deep as color 0.4, etc. The following figures showing the colors of dilutions of a highly colored water as read against the two standards show that these are real and not merely apparent differences.

Dilution of a highly colored water:

Dilution. Per cent. of Colored Water.	Calculated. Color.	Colors as Measured.		
		Nesslerised Ammonia.	Platinum. Nessler Tube.	Platinum. 600-mm. Tube.
100	2.10	2.30	(2.30[1])	...
50	1.05	1.00	(1.10[1])	...
33⅓	.70	.60	.70	...
25	.52	.40	.53	...
20	.42	.30	.43	...
10	.21	.10	.22	.20
4	.08	0	.08	.08

[1] Above the limit of color for 200-mm. tubes; the hues in these cases do not perfectly match and the results are only approximate. In practice these colors are calculated from the more accurate readings of one of the lower dilutions, or else a depth of less than 200 mm. should be used for the comparison.

It will be seen that the colors as measured by the platinum standard (calculating those above the limits of color for the depth of liquid), are strictly proportional to the quantity of coloring matter in the various dilutions, while with the nesslerised ammonia the figures differ materially from the calculations, always indicating a greater reduction in color than corresponds to the extent of dilution. Moreover, if more Nessler reagent, or a more sensitive reagent, had been employed, or if the distilled water used had contained a trace of ammonia, even though too little to be shown by direct nesslerisation, the lower figures would have been farther reduced, and still greater deviations from the calculated colors would have resulted.

Taking into account the unavoidable variations due to the imperfections of the nesslerised-ammonia standard, the two standards agree strikingly, and it would hardly be possible to secure a standard free from the defects of the nesslerised ammonia which would at the same time better agree with it at all points. This is a most important point in connection with the extensive records of color already obtained with the use of the older standard.

Conclusions.

The nesslerised-ammonia standard of color, although the best heretofore proposed, is open to very serious objection owing to the great range in the standard colors with comparatively slight variations in manipulation, the colors of the lower standards depending quite as much upon the quantity and quality of Nessler reagent employed as upon the ammonia; and also to the fact that the numbers expressing the colors are not directly proportional to the colors themselves. It also fails to provide a place for the large number of waters having colors less than that of nesslerised distilled water.

In the *platinum color-standard* now proposed the above imperfections are entirely overcome. The necessary standards are easily prepared of exact strength, and are unimpeachable in the constancy and permanency of their colors, which are not affected by any reasonable variation in the manipulation employed. The hue of the standards can be made to match that of natural waters allowing more accurate comparisons than are possible with nesslerised ammonia, and, within reasonable limits, the figures obtained are directly proportional to the actual colors.

The figures obtained are approximately equal to those of the nesslerised-ammonia standard, differing only so much as is necessitated by the imperfections of the latter, so that the adoption of the platinum standard will make the minimum disturbance with the data already accumulated.

In conclusion, I wish to acknowledge my obligation to Prof. T. M. Drown, of the Massachusetts Institute of Technology, for many valuable suggestions, and also to Mr. H. W. Clark for the assistance he has given in these investigations.

LAWRENCE EXPERIMENT STATION, MASSACHUSETTS STATE BOARD OF HEALTH.

THE CONDENSATION-PRODUCTS OF FURFUROL WITH AROMATIC BASES.

BY G. J. L. DE CHALMOT.

Furfurol, aniline and aniline hydrochloride when mixed together, whether in solution or not, react upon one another with the formation of a violet-red crystalline compound. Stenhouse[1] was the first to examine this product with care. He showed that it was formed by the direct combination of one molecule each of furfurol, aniline and aniline hydrochloride, and that the composition of the compound could be represented by the formula $2C_6H_7N.C_5H_4O_2.HCl$, there being no splitting off of water. A similar compound is formed if toluidine be substituted for aniline. From these dyestuffs he was able by means of ammonia to prepare basic substances, but only in the form of impure, yellowish brown, gummy products which could be preserved only when protected from the light and kept in a vacuum over sulphuric acid.

H. Schiff[2] investigated the reactions of other bases with furfurol, and found that various aromatic amines, amido acids and acid amides could take the place of aniline in this reaction. He always obtained a red or violet-colored product. Of the aliphatic amines only urea and allantoïn would take part in the reaction. Schiff concluded that furfurol, in contradistinction to the aromatic alde-

[1] Ann. Chem. (Liebig) **156**, 197. [2] Ibid. **201**, 355; **239**, 349.

hydes, does not form the usual condensation-product with organic bases. Prof. Wallach and I[1] have, however, obtained these ordinary condensation-products with the different amines, according to the following reactions:

$$R.NH_2 + C_5H_4O_2 = RN : C_5H_4O + H_2O, \text{ and}$$
$$2R' : NH + C_5H_4O_2 = (R'N)_2.C_5H_4O + H_2O.$$

Nevertheless, the bases which are the products of this condensation possess properties entirely different from those of the bases before mentioned, and in every way behave themselves like simple condensation-products, being very easily transformed back into aldehyde and base by the action of dilute acids or even by boiling with water. The decomposition of the dyes is not of such a simple character, and Schiff on this account concluded that they could not be simple condensation-products. Nor did he think their formation was to be explained by the view that there was a rupture of a double union in the furfurol nucleus, since aniline is not capable of uniting itself to the nucleus of pyromucic acid or its nitrogen derivatives. Heated with pyromucic acid and zinc chloride at 160° C., aniline yields as the only condensation-product pyromucanilide. That the oxygen atom of the furfuran nucleus took no part in the formation of the base, Schiff proved in like manner, drawing the conclusion that a furfuran-diphenylmethane nucleus is present in these dyes. He therefore put forward to represent the composition of furfuraniline, the formula[2]

$$CH\begin{cases} C_4H_3O \\ C_6H_4.NH_2.HCl. \\ C_6H_4.NH_2.H_2O \end{cases}$$

This assumption is very plausible, but it must be remembered that Schiff could bring forward no proof of it, since he was unable to prepare the free furfuran-diphenylmethane.

[1] *Vide* author's Inaug. Diss., Göttingen, 1891.

[2] There is, if this formula be correct, similarity between the formation of furfuraniline and that of leuco-malachite green from benzaldehyde and dimethylaniline in the presence of zinc chloride. Yet a tetramethylfurfuraniline salt would not be analogous to malachite-green, as can easily be seen by a comparison of the formulæ:

I. $CH\begin{cases} C_4H_3O \\ C_6H_4.N(CH_3)_2.HCl. \\ C_6H_4.N(CH_3)_2.H_2O \end{cases}$ II. $C\begin{cases} C_6H_5 \\ C_6H_4.N(CH_3)_2 \\ C_6H_4.N(CH_3)_2.Cl \end{cases}$.

A compound which differs from leuco-malachite-green only in the fact that it contains, in the place of three benzene nuclei, two of benzene and one of furfuran, was prepared by Otto Fischer (Ann. Chem. [Liebig] **206**, 141) by heating furfurol with diphenylamine and zinc chloride: this compound is, however, colorless.

It therefore seemed to me worth while to test the formula proposed by Schiff. When working in the laboratory of the Johns Hopkins University, this investigation was begun, but the work was soon after unavoidably interrupted. I herewith publish such results as have been so far obtained, though I regret that I shall not be able to continue the work in the immediate future.

The simple condensation-products obtained by Wallach and myself can readily be distilled under diminished pressure: the dye-forming bases, on the other hand, cannot be distilled without decomposition, even in a vacuum. My results accord in this respect with the statements of Schiff. The preparation of the dye-forming bases in a pure condition was, after repeated attempts, given up. Schiff tried in vain to prepare the free furfuran-diphenylmethane, but as he had always worked with the base in the presence of water and as the latter substance reacts upon the dye-forming bases and their derivatives, decomposing them with ease, it seemed not impossible that in solutions free from water better results might be obtained. My first attempt was to diazotise the acetate by means of amyl nitrite, according to the method of Knoevenagel,[1] the acetate being moderately soluble in alcohol, especially in the presence of a little glacial acetic acid.

A solution of the acetate in absolute alcohol containing acetic acid was therefore treated with the theoretical amount of amyl nitrite. Even after standing 24 hours, there was no precipitation on the addition of ether. A small amount of a gummy product was gradually deposited, but this was insoluble in water and did not explode when heated on platinum foil. The color of the solution had, while standing, changed from a deep red to a dirty brown. No diazo-product could be isolated.

The method, devised by Liebermann and Scheidung[2] and improved by E. and O. Fischer,[3] by which the amido group may be directly replaced by a hydrogen atom, was also employed. The hydrochloric-acid salt of the toluidine compound was used, and this was ground, in small quantities at a time, with concentrated sulphuric acid. By this action there was formed a green solution which contained the base, still undecomposed, for the addition of alcohol restored the red color. This solution in sulphuric acid was then diazotised by means of nitrous acid and, on being mixed with absolute alcohol, the product gave rise to a

[1] Ber. d. chem. Ges. **23**, 2995. [2] Ibid. **8**, 1108. [3] Ibid. **9**, 899.

brisk evolution of nitrogen and aldehyde—a result Schiff also obtained in his attempts to form the diazo-compound. I was unsuccessful, as he was, in my attempts to obtain a neutral product from the alcoholic solution: the compound had suffered a deep-seated decomposition.

After having obtained these negative results, I determined to investigate the products of the decomposition of the substance more closely; this I have only begun.

In the formation of furfuraniline from furfurol, aniline and aniline hydrochloride there is no separation of water, as one would expect. Schiff repeatedly declares in his papers that there is no reason for believing water of crystallisation present in the base, but is of the opinion that it is combined with one of the amido groups.[1] As this supposition did not seem to me very probable, the paratoluidine compound was heated to a temperature of 100° to 105° C. The compound did not at first show any signs of decomposition, but after some hours began to give off a strong pungent odor. Constant weight was not reached after fourteen hours' heating, yet after a few hours the loss was slight.

1.4672 grams of base, twice recrystallised, was heated at 100°–105° C., and weighed at the end of each hour. During the eighth hour the loss in weight was 0.0011 gram; during the ninth, 0.0016 gram. During the nine hours the total loss in weight was 0.0793 gram = 5.40 per cent. One molecule of water would correspond to 5.17 per cent. The analysis of the dried substance gave the following results:

	Calculated for $C_{19}H_{20}N_2O.HCl$.	Found. I.	Found. II.
C	69.51	69.67	69.25
H	6.40	6.88	6.72

Examined with the microscope, the crystals, which had originally appeared well-formed, transparent, violet-colored needles, were found to have become shapeless and opaque, after being heated for nine hours. The violet color had changed to a reddish tint. The dried substance behaves itself towards solvents, however, precisely like the crystalline compound. It seems to me that these facts justify the view that water of crystallisation is present in the compound, and that the conception of water being combined with one of the amido groups is not supported in any way by the facts.

[1] See Schiff's formula, p. 311.

The compound is decomposed by heating, the furfuran nucleus being broken down. Of the benzene nuclei one at least remains undecomposed. Furfuran-paratoluidine hydrochloride was heated in a tube at 200°, and yielded, in addition to dark-colored decomposition-products, colorless crystals. An aqueous extract yielded a precipitate with platinic chloride; with furfurol and acetic acid it became red. The product of the heating was therefore an aromatic base. It is then of the greatest importance, in order to establish the constitution of the dye-forming base, to determine which of the aromatic bases is here produced. If the view that the substance contains a furfuran-diphenylmethane nucleus be correct, we might expect to obtain a compound containing either a diphenylmethane nucleus, or, in the case of furfuran-toluidine, one containing two alkyl radicles in the place of benzene hydrogen atoms.

Furfurol has no action upon dimethylaniline or its hydrochloric-acid salt. From this Schiff concluded that in the formation of the dye, one molecule each of base and furfurol must at first unite, with splitting off of water, to form the usual condensation-product; this then combines with another molecule of base. Wallach and I have shown that the formation of these condensation-products with the aromatic bases does actually take place. If, then, the compound $C_6H_5.N:C_5H_4O$ can form with dimethylaniline a dye of the composition $CH\begin{cases} C_6H_4.NH_2 \\ C_6H_4.N(CH_3)_2.HCl.H_2O \\ C_4H_3O \end{cases}$, this would be a strong argument in favor of Schiff's furfuraniline formula. This reaction I herewith desire to reserve for investigation.

THE TRANSPORTATION OF SOLIDS IN A VACUUM BY THE VAPORS OF METALS.

By H. N. Morse and John White, Jr.

Further experiments[1] on the transportation of substances in a vacuum by the vapors of zinc, cadmium and magnesium have shown us that our explanation of the phenomenon was entirely erroneous.

[1] This Journal **11**, 258, 348.

It has since been found that other substances than the oxides and sulphides, such as barium carbonate and powdered porcelain can be transported with equal facility and without change of composition; moreover, that the insertion of porous plugs of asbestus, which allow the metallic vapors to pass, will effectually stop all the solids which were experimented with. It appears, therefore, that the transportations which we described must have been of a mechanical nature, and not due to dissociation.

We have also examined with greater care the gas which is evolved when the oxides of zinc, cadmium and magnesium are heated in a vacuum with their respective metals, and found it to be quite pure nitric oxide. In the original experiments the oxides were heated to redness in a vacuum, until they ceased to give off gas, before heating them with the metals. This precaution, it now appears, did not suffice for the complete decomposition of the small quantities of nitrate which they contained. Zinc oxide which has been heated to a high temperature in a muffle-furnace, does not give up any gas when heated with metallic zinc in a vacuum. The gas which was liberated when the oxides and metals were heated together was found to be insoluble in strong caustic potash, but readily soluble in an alkaline solution of pyrogallic acid; it was therefore too hastily concluded that the gas must be oxygen. In our later experiments this gas was found to be indifferent to phosphorus, but readily absorbed by solutions of ferrous salts. It appeared, furthermore, that freshly prepared alkaline solutions of pyrogallic acid absorb nitric oxide with considerable avidity.

To determine whether nitric oxide is readily reduced by the vapors of metallic zinc, we exhausted a tube containing some of the metal, and then filled it with the oxide. After heating the tube in a combustion-furnace for six hours, the contents were pumped out and examined. About ninety-five per cent. of the gas thus obtained was unchanged nitric oxide. In the light of this result it is easy to understand why the gas which is rapidly pumped off when zinc and zinc oxide containing some nitrate are heated together in a vacuum, should consist of pure nitric oxide, instead of a mixture of its reduction-products.

REVIEWS AND REPORTS.

STEREOCHEMISTRY.

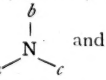
II.—*The Stereochemistry of Nitrogen.*[1]

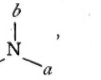
The first founder of stereochemistry was also the first to suggest a three-dimensional arrangement of the radicles attached to nitrogen. Van't Hoff[2] bases this arrangement on the fact that of the five valences of nitrogen three are apparently alike, while two differ from these in that they are active only in exceptional cases. That the three ordinary valences are alike is shown by the fact that among complex ammonias (N.*a.b.c*) there is no isomerism. This indicates that *a*, *b*, *c* are in the same plane with N; for otherwise we should have two formulæ,

and

,

which are non-superposable and represent therefore two distinct substances; whereas the plane formulæ



and


,

being superposable, are identical.

The arrangement of *a*, *b* and *c* round N is then that of the corners of an equilateral triangle round its center; always remembering that the nitrogen triangle is represented as equilateral for the same reason that the carbon tetrahedron is represented as regular, not because we know the different radicles to be at the same distance from the connecting element, but because we know not which is nearer and which farther from it.

As to the positions of the radicles *d* and *f*, bound by the two supplementary valences, we have no reason to suppose that either of these is nearer to any one of the radicles *a*, *b*, *c* than to the others. The radicles *d* and *f* must therefore be represented as equidistant from each of the three radicles *a*, *b*, *c*; so that the arrangement is determined by the position of five points, three of which are equidistant from one another and from each of the other two. Now three points cannot be equidistant from each of two other points which are in the same plane with them; hence a

[1] For "Stereochemistry of Carbon" see This Journal **13**, 496, 573; **14**, 58.
[2] Ansichten über die organische Chemie (Brunswick, 1881), p. 79

three-dimensional arrangement is necessary. The arrangement is shown in perspective in Fig. 1, and more clearly perhaps in Fig. 2; here 1, 2, 3 are the ordinary similar valences and 4 and 5 the supplementary valences. The fact that 4 and 5 are dissimilar in that one binds negative and the other positive radicles might be represented by using a + and a — sign.[1] It cannot be represented by making one line longer than the other, because the difference is a difference of kind, not of degree merely.

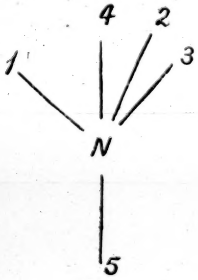


FIG. 1.

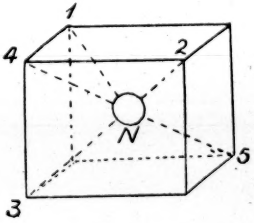


FIG. 2.

Now we have experimental proof that the arrangement of five radicles attached to nitrogen is a three-dimensional one. Le Bel[2] obtained by the action of ferments on methyl-ethyl-propyl-isobutyl-ammonium chloride, $\left.\begin{matrix}CH_3\\C_2H_5\\C_3H_7\\C_4H_9\end{matrix}\right\}$NCl, a solution optically active.[3] That is to say, the molecule in question has no plane of symmetry; therefore its components cannot all be grouped in a single plane.

Again, Van't Hoff's configuration demands the existence of two isomers NA_3BC (or NA_2B_2C), for if C occupy bond 5 (Fig. 1), bond 4 may be occupied by either B or A. In the case of dimethyl-diethyl ammonium iodide, $N(Me)_2Et\begin{matrix}Et\\I\end{matrix}$, and $NMe(Et)_2\begin{matrix}Me,\\I\end{matrix}$ there is said to be no isomerism.[4] The Figs. 3 and 4, which represent the theoretical isomers, have, however, the same plane of symmetry which may determine the identity in crystalline form; hence Van't Hoff demands further evidence of the alleged identity.

[1] Compare Behrend: Ber. d. chem. Ges. **23**, 454 and 1776; and Willgerodt's objections, J. prakt. Chem. [2] **41**, 526.

[2] Bull. Soc. chim. (Paris) [3] **4**, 613.

[3] According to this, Le Bel's view that the essential condition for the optical activity of an organic substance in solution is the presence of any asymmetric molecule must be preferred to Van't Hoff's theory that the presence of an asymmetric carbon atom is essential.

[4] V. Meyer and Lecco: Ber. d. chem. Ges. **7**, 1747; **8**, 223 and 936.

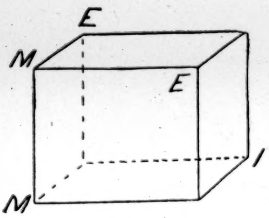


FIG. 3.

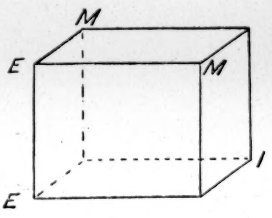


FIG. 4.

And in a parallel case, that of triethyl-benzyl-ammonium iodide, Ladenburg[1] proved in his noted controversy with Victor Meyer[2] that two isomers exist and ascribed to them the formulæ

$$N(C_2H_5)_3\begin{matrix}C_6H_5.CH_2\\ I\end{matrix} \quad \text{and} \quad N(C_2H_5)_2C_6H_5.CH_2\begin{matrix}C_2H_5\\ I\end{matrix}.$$

A difference between the substances to which these formulæ were assigned has been observed by Le Bel[3] also; and the case has been duplicated by his discovery of two isobutyl-trimethyl-ammonium chlorides.[4]

Van't Hoff's speculations foreran contemporary chemistry, so that by the time other chemists began to entertain similar views they had forgotten the original statement of them. Thus Willgerodt,[5] to whom Van't Hoff's work was evidently unknown, gave as the general formula for nitrogen compounds a solid figure derived from Fig. 1 by simply joining together the points 1, 2, 3 and joining 4 and 5 to these, forming the outline of the figure given for two carbons trebly-linked.[6] This Willgerodt called the nitrogen double-tetrahedron.

It is needless to discuss Willgerodt's explanation of certain cases of isomerism among derivatives of azobenzene said to be structurally identical, because the structural identity is apparently unproven,[7] and because the explanation itself admittedly[8] requires to be explained.

The two supplementary valences (*Burch and Marsh*).—The expression of the fact that nitrogen, which can bind five, so often binds only three monads, we have seen in Van't Hoff's formulæ; we have now to consider the explanation of this fact. An explanation of the general phenomenon of varying valence is given by Van't Hoff in the introduction to his *Ansichten*, and would be expressed in a nitrogen formula by making the distance N_4 (=N_5) greater than the distance N_1 (=N_2=N_3), Fig. 1. For the

[1] **Ber. d. chem. Ges. 10**, 43, 561, 1152 and 1634.
[2] Ibid. **10**, 309, 964, and 1291.
[3] Bull. Soc. chim. (Paris) [3] **3**, 244, and **4**, 104.
[4] Compt. rend. **110**, 144.
[5] J. prakt. Chem. [2] **37**, 449; also **41**, 291, and **42**, 127.
[6] This Journal **13**, 580.
[7] **Kehrmann and Messinger**: Ber. d. chem. Ges. **25**, 598.
[8] Willgerodt: loc. cit. **37**, 452.

particular case of nitrogen an explanation (which may possibly be extended to other elements) has been suggested by Burch and Marsh:[1] the valences apparently latent may in reality be engaged in binding together nitrogen atoms belonging to what are at present regarded as different molecules.

The molecule of ethyl-amine would then be not $NH_2.C_2H_5$, but a multiple of this, such as $C_2H_5.H_2N = NH_2.C_2H_5$ or

$$C_2H_5.H_2N - NH_2.C_2H_5 ;$$
$$\diagdown\ \diagup$$
$$NH_2.C_2H_5.$$

and if these complex molecules are dissociated by rise of temperature, the vapor of ethyl-amine should give abnormally large expansion on heating. Experiment showed an expansion 5 to 6 per cent. in excess of the normal, with contraction to the original volume on cooling. The impossibility of separating by fractional distillation mon-ethyl-, di-ethyl- and tri-ethyl-amine is due perhaps to the linking together of the different compounds by the supplementary nitrogen-valences.

Now carbon, which in combination is remarkable for the linking together of numbers of its own atoms, exhibits similar linking when free; so also with sulphur.[2] Accordingly the proof given by Burch and Marsh, that pentad nitrogen when combined has something of the self-binding power possessed by carbon and sulphur, stands in direct connection with the remarkable work of Stillingfleet Johnson,[3] whose conclusions have received independent corroboration from Thomson and Threlfall,[4] and whose researches make it probable that nitrogen when free may be formed into molecules containing more atoms than the ordinary nitrogen molecule. For the abnormal *contraction* which Thomson and Threlfall observed on passing the electric discharge through gaseous nitrogen, may be due to triad nitrogen becoming pentad,[5] just as the abnormal *expansion* of ethyl-amine vapor is said to be due to pentad nitrogen becoming triad. The stereochemical bearing of these arguments becomes clear when we consider that Van't Hoff's nitrogen figure contained within itself the prediction that the molecule of Johnson's allotropic nitrogen (if this is indeed pentad nitrogen), like the molecule, or rather the various molecules of carbon, must consist of more than two atoms, for with pentad nitrogen, as with carbon, the direction of the valences is

[1] J. Chem. Soc. **55**, 654.
[2] Van't Hoff: "Ansichten," p. 23.
[3] J. Chem. Soc. **39**, 128, 130; also "Elementary Nitrogen," London: Churchill, 1885.
[4] Proc. Roy. Soc. **40**, 329.
[5] Accepting the pole hypothesis as to the supplementary valences, the explanation of their *Activirung* would be that the opposite poles are brought into proximity by the difference of potential between the surfaces *A* and *B*; thus: (neglecting the ordinary valences)—

such that all cannot be satisfied by the union of two atoms; whereas in molecules composed of triad nitrogen the union of two atoms may evidently satisfy all the valences.

The three ordinary valences (Hantzsch and Werner).—With the publication in 1890 of a paper by Hantzsch and Werner[1] the stereochemistry of nitrogen entered on a new phase. Their theory, like the stereochemical theories of Van't Hoff, arose from the consideration of certain cases of unexplained isomerism. The isomers in question were aromatic oximes, such as the oxime of benzaldehyde, $C_6H_5.CH:NOH$, which exists in two chemically distinct forms of the same structural formula. To explain this Hantzsch and Werner began by denying that the three ordinary nitrogen valences always occupy the same plane; in cyanogen —CN and pyridin $C_5H_5:N$ the carbon valences linked with nitrogen not being in the same plane, it follows that the nitrogen valences themselves must be out of plane; in certain compounds, then, the three valences of nitrogen are directed towards three apices of a (doubtless irregular) tetrahedron, the fourth apex of which is occupied by the nitrogen atom.

From this arrangement it follows that three classes of stereo-isomers are possible:

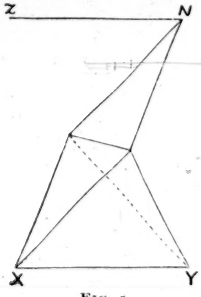


FIG. 5.

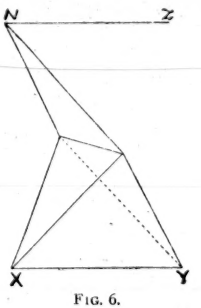
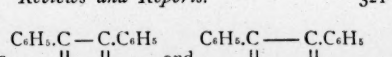


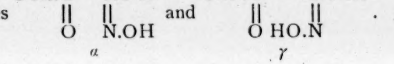
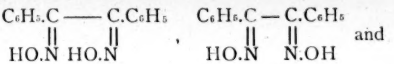
FIG. 6.

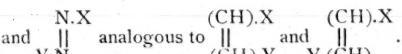
I. Type $\begin{matrix} Z.N \\ \| \\ X.C.Y \end{matrix}$ and $\begin{matrix} N.Z \\ \| \\ X.C.Y \end{matrix}$ (Figs. 5 and 6), analogous to $\begin{matrix} H.C.Z \\ \| \\ X.C.Y \end{matrix}$ and $\begin{matrix} Z.C.H \\ \| \\ X.C.Y \end{matrix}$.

Examples: Benzaldoximes $\begin{matrix} H.C.C_6H_5 \\ \| \\ N-OH \end{matrix}$ and $\begin{matrix} H.C.C_6H_5 \\ \| \\ HO-N \end{matrix}$.

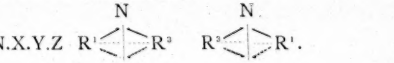
[1] Ber. d. chem. Ges. **23**, II.

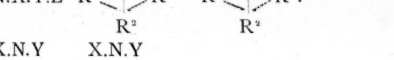
Benzilmonoximes  .

Benzildioximes  and  .

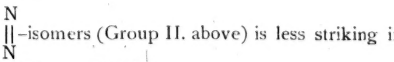
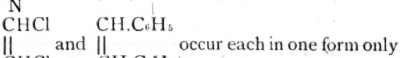
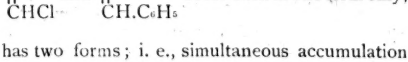
II. Type  .

No examples yet known with certainty.

III (*a*). Type  .

(*b*). Type 

No examples known.

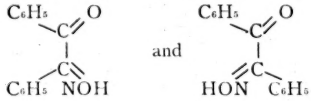
The scarcity of  -isomers (Group II. above) is less striking if we consider that  occur each in one form only, while  has two forms; i. e., simultaneous accumulation of negative and of phenyl (aromatic) groups favors occurrence of isomerism among carbon derivatives (as among the nitrogen compounds of Group I—the oximes); whereas, even among carbon derivatives isomers may be lacking in compounds possessing analogous constitution, but lacking the right combination of groups.

As to the absence of isomers of Group III (NXYZ), this is accounted for by the theory that the three nitrogen valences are all in one plane except when diverted by special cause. If in any case such special cause exists, optically active isomers[1] may be expected.[2] Thus Hantzsch and Werner give a general theory leading us to expect the occurrence of those cases of isomerism

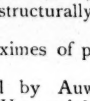
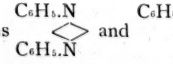
[1] Bischoff is trying to prepare such isomers: Ber. d. chem. Ges. **23**, 1967.
[2] See ante, p. 316.

which actually exist, but also of many others; and then to account for the non-existence of these latter, they give special subsidiary theories.

Opposition to the theory arose from the belief that not the presence of nitrogen but the presence of two singly-linked carbons was the necessary condition for the occurrence of isomerism among structurally identical oximes, and the formulæ



had been proposed by Auwers and Meyer,[1] who thought that in this case relative rotation[2] of the singly-linked carbon atoms did not take place. As to the benzaldoximes, these, it was said, were structurally, not stereochemically, different. The improbability of the latter assertion has been demonstrated by the work of Goldschmidt[3] and of Hantzsch,[4] as Meyer[5] now admits; and the former theory was crushed by the discovery of structurally identical ketoximes containing no $\begin{matrix}C\\|\\C\end{matrix}$ group, viz. the oximes of parachlor-benzophenone, $C_6H_5.CO.C_6H_4.Cl$, discovered by Auwers and Meyer[6] themselves, and others discovered by Hantzsch.[7]

Meyer, however, had based his opposition on other grounds also, maintaining[8] that though the three valences of nitrogen may be diverted from one plane by adequate force, such force is lacking in cases where Hantzsch and Werner base their theory on its existence; that it is the absence of any such diverting force (and not the absence of negative groups) which accounts for the fact that azo-benzene exists in but one form, viz.  , and not in the two forms  (see isomers of type

[1] Auwers: "Entwicklung der Stereochemie," p. 53 et seq.; see also Meyer: Ber. d. chem. Ges. **23**, 592.
[2] See ante, **14**, 59.
[3] Ber. d. chem. Ges. **22**, 3109, and **23**, 2163, 2746. For Beckmann's papers on the subject see Ibid. **20**, 2766; **22**, 429, 514, 1531, 1588; **23**, 1680, 3319, 3331.
[4] Ibid. **24**, 13.
[5] Ann. Chem. (Liebig) **264**, 16.
[6] Ber. d. chem. Ges. **23**, 2063.
[7] Ibid. **23**, 2322.
[8] Ibid. **23**, 607.

II above). Further, where there is force adequate to cause divergence, the direction in which it acts is constant; so that, in the case of benzil-dioxime, if phenyl attracts hydroxyl, the formula would be only $\begin{matrix} C_6H_5.C - C.C_6H_5 \\ \| \quad\quad \| \\ HO.N \quad N.OH \end{matrix}$; and if phenyl repels hydroxyl, the formula could be only $\begin{matrix} C_6H_5.C \text{———} C.C_6H_5 \\ \| \quad\quad\quad \| \\ N.OH \quad HO.N \end{matrix}$; in either case, therefore, we have but one formula for the oxime.

Hantzsch and Werner[1] admit that since the three nitrogen valences are originally in one plane there must be in the ketoximes a special cause for their divergence, but the divergence need not be always in the same direction, for in the formation of a ketoxime addition first takes place: $>C=O + H_2N.OH = >C<^{OH}_{NH.OH}$; and the hydroxyl so formed may take the place which would otherwise be taken by the hydroxyl of the hydroxylamine; this latter hydroxyl is thus forced into an unfavorable position, in which it may remain even after the splitting off of H_2O. But again Auwers and Meyer[2] objected that the isomerism, the production of which is ascribed to nitrogen, occurs only among hydroxyl-amine derivatives, and may be better accounted for by the formulæ $\overset{a}{\underset{b}{C}}=N-\overset{H}{O}$ and $\overset{a}{\underset{b}{C}}=N-O.$

These formulæ were met by several counter-objections[3] which seem fatal. Thus:

1. They do not represent two distinct molecules, but two phases in the rotation of the atoms of the same molecule; for why should not H rotate round $=N-O-$?

2. The existence of two structurally identical nitrogen-ethers is unexplained; $\begin{matrix} X \\ Y \end{matrix}>C\overset{O}{\wedge}NR$ cannot be derived in two forms from $\begin{matrix} X \\ Y \end{matrix}>C=N-\overset{H}{O}$, whereas by diverting the nitrogen valences we have at once $\begin{matrix} X \\ Y \end{matrix}>C\overset{O}{\diagup}\underset{\diagdown}{N}\overset{R}{\diagup}$ and $\begin{matrix} X \\ Y \end{matrix}>C\overset{O}{\wedge}\underset{R}{N}$.

[1] Ber. d. chem. Ges. **23**, 1243.
[2] Ber. d. chem. Ges. **23**, 2403.
[3] Hantzsch and Werner: Ibid. **23**, 2764. See also Ibid. **24**, 3511, and the answer of Auwers and Meyer: **24**, 4226.

The theory of Behrend is also discussed by Hantzsch and Werner. Behrend[1] assumes the existence in the nitrogen atom of two poles of opposite sign (corresponding to the two supplementary valences) and ascribes to the three benzil-dioximes the formulæ

$$\begin{array}{l} \overset{-}{\text{C}_6\text{H}_5.\text{C}:\text{NOH}} \\ \quad\vert\ \overset{+}{} \\ \underset{+}{\text{C}_6\text{H}_5.\text{C}:\text{NOH}} \end{array} \qquad \begin{array}{l} \overset{-}{\text{C}_6\text{H}_5.\text{C}:\text{NOH}} \\ \quad\vert\ \overset{+}{} \\ \underset{-}{\text{C}_6\text{H}_5.\text{C}:\text{NOH}} \end{array} \qquad \begin{array}{l} \overset{+}{\text{C}_6\text{H}_5.\text{C}:\text{NOH}} \\ \quad\vert\ \overset{-}{} \\ \underset{+}{\text{C}_6\text{H}_5.\text{C}:\text{NOH}} \end{array}$$

But this theory also is rejected; for, *inter alia*, it fails to account for the isomerism of the benzaldoximes.

Besides combatting the opinions of others, Hantzsch and Werner have sought positive evidence in favor of their own, and this in two ways: Firstly, by trying to prepare the isomers foreseen by their theory; secondly, by trying to obtain the reactions which the theory attributes to each isomer.

I. *a.* Isomers other than oximes have been found only among the hydrazones[2] $\begin{matrix} \text{XCY} \\ \Vert \\ \text{N}-\text{NH.C}_6\text{H}_5 \end{matrix}$ and $\begin{matrix} \text{XCY} \\ \Vert \\ \text{C}_6\text{H}_5.\text{HN}-\text{N} \end{matrix}$.

Substances such as N.X.Y.Z and $\begin{matrix} \text{X} \quad \text{Z} \\ \text{C}=\text{N} \\ \text{Y} \end{matrix}$ could not be prepared in more than one form. Thus Kraft[3] tried in vain to break up ethyl-toluidine, $\text{N}\begin{matrix}\diagup\text{C}_2\text{H}_5 \\ -\text{CH}_2.\text{C}_6\text{H}_5 \\ \diagdown\text{H}\end{matrix}$, into two optically active isomers; but he found that the method tried—the crystallisation of the tartrate in presence of coniine tartrate—was unsuccessful also when applied to an inactive base containing an asymmetric carbon atom, so that the experiment shows only the difficulty, not the impossibility, of obtaining isomeric ammonia derivatives.

b. Among oximes space-isomerism is possible if the radicles attached to $>\text{C}=\text{N.OH}$ are any two of the following: H, C_6H_5, $\text{C}_4\text{H}_3\text{O}$, $\text{C}_4\text{H}_3\text{S}$, $\text{CH}_3.\text{C}_6\text{H}_4$, $\text{C}_6\text{H}_4.\text{Cl}$, $\text{C}_2\text{H}_3\text{O}.\text{C}_6\text{H}_4$.[4] Methyl, and probably alkyls generally prevent this isomerism.[5]

[1] See ante, p. 316.

[2] Ber. d. chem. Ges. **23**, 2769; **24**, 3511. Compare Auwers and Meyer and their collaborators, Ibid. **23**, 1574, 3617; **24**, 4225.

[3] Ibid. **23**, 2780. Compare Bischoff, Ibid. **23**, 1967.

[4] To these must be added a variety of others if Werner (Ber. d. chem. Ges. **25**, 27) is right in explaining the isomerism observed among hydroxamic acid derivatives according to his theory. There are at least twenty-seven of these compounds which occur in more than one modification (Lossen: Ber. d. chem. Ges. **25**, 433); but Lossen finds that some of these occur in three modifications, and, besides, he distrusts the methods by which Werner arrives at his conclusions.

[5] Kehrmann (J. prakt. Chem. [2] **42**, 134) had suggested that the reason V. Meyer could not prepare isomeric diacetyl-dioximes was because in the process of formation the unfavored turns into the favored configuration, while the more unwieldy benzil-derivatives require stronger impulses to effect conversion. But Hantzsch says it is not so much the space occupied by the radicles which is of moment as their configuration, a factor at present undetermined. For the oxime of benzaldehyde exists in two forms, that of aceto-phenone in one form only, although the latter has in place of hydrogen the larger methyl.

II. *a*. Of two aldoximes, $\begin{matrix}XCH\\ \|\\ N.OH\end{matrix}$ and $\begin{matrix}XCH\\ \|\\ HO.N\end{matrix}$, the former should yield the nitrile $\begin{matrix}XC\\ \|\|\|\\ N\end{matrix}$ more readily than the latter. Experiment confirms this.[1]

b. To ketoximes Beckmann's transformation was applied—a transformation which may take place in either of two ways: $\begin{matrix}X\\ Y\end{matrix}\!>\!C\!=\!N.OH \rightarrow X.C\!-\!N\!<\!\begin{matrix}H\\ Y\end{matrix}$ or $Y.C\!-\!N\!<\!\begin{matrix}X\\ H\end{matrix}$. Whether it is X or Y which changes its place should depend on which is nearer to the hydroxyl:

$$\begin{matrix}X\\ Y\end{matrix}\!>\!C\!=\!\overset{OH}{N} \rightarrow \overset{O}{YC}\!-\!\overset{X}{NH}\text{; and } \begin{matrix}X\\ Y\end{matrix}\!>\!C\!=\!\underset{OH}{N} \rightarrow \underset{O}{XC}\!-\!\underset{Y}{NH}.$$

And of the three benzil-dioximes— I. $\begin{matrix}C_6H_5.C\text{———}C.C_6H_5\\ \|\qquad\qquad\|\\ N.OH\quad HO.N\end{matrix}$,

II. $\begin{matrix}C_6H_5.C\text{———}C.C_6H_5\\ \|\qquad\qquad\|\\ HO.N\quad HO.N\end{matrix}$, III. $\begin{matrix}C_6H_5.C-C.C_6H_5\\ \|\qquad\|\\ HO.N\quad N.OH\end{matrix}$—

that one (III) which the least readily yields the anhydride should the most readily undergo the transformation of Beckmann. This also is confirmed by experiment.[2]

To distinguish structurally identical nitrogen compounds $\begin{matrix}X.C.Y\\ \|\\ Z.N\end{matrix}$ and $\begin{matrix}X.C.Y\\ \|\\ N.Z\end{matrix}$ by name Hantzsch[3] uses the prefixes *syn-* and *anti-*, which indicate the position of the radicle Z with regard to that one of the radicles X and Y which is capable of intramolecular reaction with Z and the name of which is to immediately follow the prefix. Thus:

$\begin{matrix}C_6H_5.C.H\\ \|\\ HO.N\end{matrix}$ Benz-anti-aldoxime. $\qquad$ $\begin{matrix}C_6H_5.C.H\\ \|\\ N.OH\end{matrix}$ Benz-syn-aldoxime.

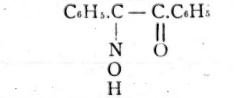
In the case of dioximes the prefixes refer to the two hydroxyl groups, and where these have the asymmetrical position the term *amphi-* is used.

The oximes of diphenyl-glyoxal are then

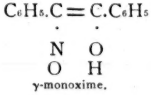
$\begin{matrix}C_6H_5.C\text{———}C.C_6H_5\\ \|\qquad\qquad\|\\ N.OH\quad HO.N\end{matrix}$ Diphenyl-syn-glyoxime. $\quad$ $\begin{matrix}C_6H_5.C\text{——}C.C_6H_5\\ \|\qquad\|\\ HO.N\quad N.OH\end{matrix}$ Diphenyl-anti-glyoxime. $\quad$ $\begin{matrix}C_6H_5.C\text{——}C.C_6H_5\\ \|\qquad\|\\ N.OH\quad N.OH\end{matrix}$ Diphenyl-amphi-glyoxime.

[1] Ber. d. chem. Ges. **23**, 25; **24**, 18. [2] Ibid. **24**, 23. [3] Ibid. **24**, 3479.

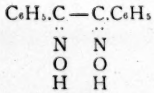
Hantzsch and Werner have done for the stereochemistry of nitrogen what Wislicenus did for the stereochemistry of carbon. They have rendered possible a systematic experimental investigation of the subject, and have themselves already pushed this investigation in many directions. Their theory is at present in possession of the field; but not in undisputed possession. Its origin was, as we have seen, due to the alleged existence of isomerism among structurally identical oximes, especially benzil-oximes. Now Claus[1] maintains that structurally identical benzil-oximes do not exist, and suggests the formulæ



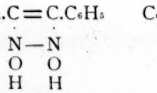
α-monoxime.



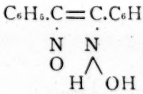
γ-monoxime.



α-dioxime.



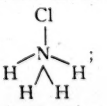
β-dioxime.



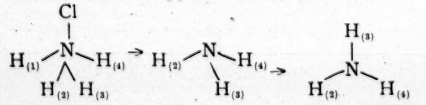
γ-dioxime.

This suggestion threatens the very base of the whole theoretical structure built up by Hantzsch and Werner, Auwers and Meyer. The latter[2] seek to prove that the threat is vain, but are constrained to admit that stereochemistry has not yet shown why the more stable of the two benzil-monoximes should on further treatment with hydroxylamine yield the most unstable of the three dioximes (γ-monoxime yields γ-dioxime, see ante, p. 321). Their opposition has been met by Claus,[3] who promises experiments on the subject shortly.

Further, the Hantzsch-Werner theory does not cover the whole field. The problem of quinquivalent nitrogen is untouched by it. On this Bischoff[4] promises investigations, and suggests for NH_4Cl a formula in which the four hydrogen atoms are disposed at the base of a pyramid of which the chlorine occupies the apex—



while for NH_3 he retains the symmetrical formula in a single plane. The transition is supposed to take place thus:



[1] J. prakt. Chem. [2] **44**, 312.
[2] J. prakt. Chem. **45**, 1, and 377.
[3] Ber. d. chem. Ges. **24**, 3267.
[4] Ber. d. chem. Ges. **23**, 1967.

Vaubel[1] has attacked the problem in a new way. He assumes that the carbon atom has the form of a regular tetrahedron, and that the atoms of all elements have the same specific gravity, so that the volume of the nitrogen atom is to that of the carbon atom as the atomic weight 14 is to the atomic weight 12. Calling the side of the carbon tetrahedron unity, its volume is $\frac{1}{12}$, and the volume of the nitrogen atom therefore $\frac{1}{12} \times \frac{14}{12} = \frac{7}{72}$. Further, in order that the nitrogen atom may replace a carbon atom in the benzene ring (Baeyer's rejected formula[2]) it must have an angle of 60° and sides equal to those of the carbon tetrahedron; and in order that it may replace two carbons in the ring (see Fig. 11) it must have a side equal to 1.732. To satisfy these hypotheses (which we will not here discuss) Vaubel proposes the form of which side-views are shown in Figs. 7 and 8.

Another view is seen in the formula for NH_4Cl (Fig. 9).

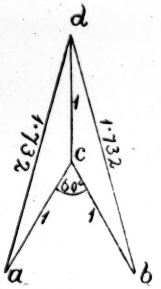


FIG. 7.

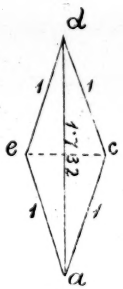


FIG. 8.

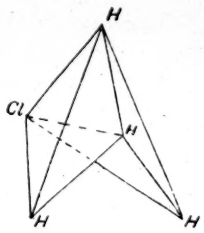


FIG. 9.

A number of illustrations are given by Vaubel to show how the form chosen is adapted to represent the linkage of nitrogen in various compounds; the formulæ for the C≡N— group and for pyrrol will convey a sufficient idea of this. (Figs. 10 and 11.)

It will be seen that the division into three ordinary valences (*A*, *B*, *D*; Fig. 7) and two supplementary valences (*E*, *C*) is retained; but seeing that the supplementary are presumably weaker than the ordinary valences, it is unfortunate that the formula should represent *E* and *C* as nearer to the center of gravity of the atom than *A*, *B* and *D*.

[1] "Das Stickstoffatom." Giessen: E. Ottmann, 1891.

[2] The formula (which Vaubel published as new in 1891 [J. prakt. Chem. [2] **44**, 137]) was proposed by Baeyer in 1888 (Ann. Chem. (Liebig) **245**, 124), only to be rejected by him in favor of the formula shown in Plate I. (ante Vol. 13 opposite p. 578). Either formula lends itself to the argument given above. The origination of the formula shown in the plate is mistakenly attributed by Vaubel to Loschmidt.

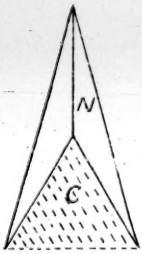


FIG. 10.

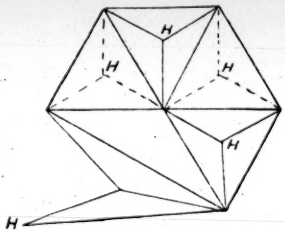


FIG. 11.

Conclusion.

The progress of the stereochemistry of nitrogen is naturally slow, owing to the relatively few cases of unexplained isomerism among nitrogen compounds; it is aided, however, by the knowledge already gained as to the stereochemistry of carbon, which has proved a useful guide in the search for new nitrogen isomers.

These outlines of stereochemistry cannot close without mentioning that, of the chemists who have considered the subject on general grounds, some have accorded but faint praise to such speculations; others, a more emphatic form of condemnation. Berthelot[1] maintained that it was of little use to theorise as to atomic arrangement without taking atomic motion into account; Kolbe[2] scoffed; Fittica[3] despaired. Claus[4] considers that while the physical properties of a substance depend to some extent on the arrangement of the atoms in the molecules, the evidence is altogether insufficient to show that, as regards chemical properties, this factor is of any weight compared with the specific nature of the atoms. Ostwald[5] admits that we are justified in attempting to explain the chemical properties of molecules by the arrangement of their atoms, but thinks[6] the question so complicated that this will prove to be but one factor among many; that we shall therefore more rapidly gain an insight into the problem of isomerism if we abandon geometrical representations and confine ourselves to "clear and necessary hypotheses."

[1] Bull. Soc. chim. (Paris) [2] **23**, 338.
[2] J. prakt. Chem. [2] **15**, 473; **23**, 489.
[3] "The form and arrangement of atoms will probably remain for ever unknown."—Jahresbericht, 1888, p. 87.
[4] J. prakt. Chem. [2] **42**, 266; **45**, 12.
[5] "Grundriss der allgemeinen Chemie" (Leipzig: Engelmann, 1889), p. 206.
[6] Ztsch. phys. Chem. **9**, 220.

Note.

Books.—A bibliography is in preparation. For the work on carbon, Van't Hoff's "Dix années,"[1] or its translation[2] by Marsh, is of most importance to the student. These reports, which aim at supplying only the briefest possible review of the whole subject, will be reprinted in pamphlet form in the hope that they may prove useful as a text-book.

Models.—No nitrogen models are at present in general use. For private study, the carbon models made by joining four short pieces of rubber-tubing to a common center, and supplied by Schneck, Königsberger, and Mandl, Breitensee near Vienna, are very good.

The models ("solid formulæ") which I recently described[3] will be supplied according to samples approved by me by Messrs. James Queen & Co., Chestnut Street, Philadelphia.

ARNOLD EILOART.

NOTES.

A. W. von Hofmann.

August Wilhelm von Hofmann, the distinguished professor of chemistry in the University of Berlin, died on the 5th of May. He was born April 8, 1818, in Giessen, a city that will always be remembered as the seat of that first chemical laboratory in which Liebig wrought such great results. Hofmann entered the University of Giessen in 1836 without a clear plan as to his future work. He soon, however, turned to the law, and later became interested in chemistry, probably through the influence of Liebig. He was a student of Liebig and afterwards his assistant. His first investigation was published in 1841, and treated of the volatile bases of coal-tar. In this work he proved the presence of aniline and quinoline in coal-tar. A later investigation was on the metamorphoses of indigo, and in this he showed that hydrogen can be replaced by chlorine.

In 1845 Hofmann left Giessen, and became privatdocent in Bonn, where he lectured on Agricultural Chemistry. From Bonn he went to England to take charge of the new Royal College of Chemistry, an institution modeled after the laboratory which was so successful in Giessen. In 1853 he became professor of chemistry

[1] Ante **13**, 497. [2] Ibid. **13**, 579, note 2. [3] This Journal **13**, 559.

in the Royal School of Mines, still remaining at the head of the College of Chemistry. In 1864 Hofmann was invited to Bonn to build a university laboratory and to become its director. Before he could take charge of the new laboratory at Bonn, he was called to Berlin, in 1865, as Mitscherlich's successor, and there he remained until his death. For many years he was active in chemical work, though during the last few years of his life he was much less active than formerly. To a very remarkable degree he retained his interest in the progress of chemistry to the last, and it appears that at the time of his death he was engaged upon an investigation on the isonitriles. The last publication bearing his name is one entitled "Ueber polymeres Methylsenföl," which appeared in the number of the Berichte of March 28, 1892. At the end of the brief article he says: "I hope after the Easter vacation to communicate to the Society details concerning these compounds." There are few indeed who have kept their hands to the chemical plough for over fifty years!

There is no question that Hofmann exerted a powerful influence upon the chemists of the last half-century, and that his work contributed largely to the advance of the science. His researches on aniline and similar bases were extraordinarily fruitful from the point of view both of pure science and of chemical industry. They led to the present conception of the constitution of aniline, so far as its relation to ammonia is concerned, and formed an important part of the foundation of that which is called "modern chemistry." On the other hand, the dyestuff industry owes an enormous debt to him. In 1858 he obtained fuchsine by treating aniline with carbon tetra-chloride, and to the investigation of this compound he devoted many years. Among his other most important investigations should be mentioned those on guanidine, formic aldehyde, iso-nitriles, mustard-oils, the alkaloids, the phosphine bases, etc.

He has received abundant evidence of the esteem in which he was held by the chemical world as well as by the world at large. Honor after honor has been paid him, the culmination being reached in the celebration of his 70th birthday, April 8, 1888, and of the fiftieth anniversary of his doctorate, August 9th, 1891.[1]

I. R.

[1] The writer of this notice is largely indebted to an article in the Chemiker-Zeitung (Vol. 16, No 38).